NIM B
**Beam Interactions
with Materials & Atoms**

Measurements of low radioactive contaminations in lead using bolometric detectors

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Bolometric detectors made with samples of crystalline and polycrystalline lead have been operated to measure their internal radioactivity due to ^{210}Pb. It has been found that contaminations of hundreds of becquerels per kilogram are present in commercial low radioactivity lead and that these contaminations can be reduced by an order of magnitude by crystallisation. A low activity of a few hundreds of millibecquerels per kilogram still persists in specially prepared low radioactivity lead. No evidence for contamination is on the contrary found in a 2000 year old lead sample from a sunk Roman ship, at a level of less than 20 millibecquerel per kilogram.

1. Introduction

Recent searches on rare events like double beta decay [1] or interactions of solar neutrinos [2] and dark matter particles [3] have stimulated interest in the measurement of intrinsic radioactive contaminations of detectors and shielding materials. If these contaminations are in the form of long living nuclides like e.g. ^{235}U, ^{238}U, ^{232}Th and ^{40}K, one can make use of mass spectroscopy methods, which achieve sensitivities up to a few parts per trillion in many solid materials [4–6]. The accuracies of these destructive techniques are, however, insufficient to determine contaminations of nuclides of shorter lifetimes, like many members of the radioactive families which break secular equilibrium or cosmogenically generated nuclei.

Nondestructive methods to reveal these contaminants are based on α, β and γ spectroscopy. The first two normally allow to investigate only a limited volume at the surface of the sample, while the efficiency of the last one is often low, thus requiring long measuring times. It has, however, been recently demonstrated that α spectroscopy can be successfully performed on the entire bulk of the sample by thermal detection [7].

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This technique, suggested since 1984 [8,9] and largely implemented recently [10,11], is based on the fact that the heat capacity of a sufficiently cold diamagnetic and dielectric crystal decreases with the cube of the ratio T/T_D between operating and Debye temperatures. In a suitable refrigerator it can become so small that even the tiny energy delivered by a single particle can give rise to a measurable increase of temperature. In recent experiments on double beta decay of ^{130}Te [7,12] carried out underground, TeO_2 crystals of masses up to 340 g, heavily shielded against local background, have been operated at temperatures around 10 mK as thermal detectors of their own radioactivity. The spectra of background counting rates show absence of α peaks due to internal radioactivity of ^{238}U and ^{232}Th chains, with sensitivities of 10^{-12} g/g on the contaminations of these parent nuclei, similar to those or even better than those reachable with mass spectroscopy [6]. The sensitivity to radioactive contaminants of shorter lifetimes which break secular equilibrium is obviously even larger: we have found for instance a contamination of ^{210}Po as low as $(3.9 \pm 0.1) \times 10^{-20}$ g/g. The FWHM energy resolution of our thermal α spectrocopy is around 10 keV, similar to those of surface detectors. It could be better with thermal detectors of lower specific heat: since we needed a material containing ^{130}Te we were forced to choose TeO_2, which has rather modest thermal properties. Finally we would like to note that thermal detectors reveal, in addition to the α-particle,

also the nuclear recoil [7]. As a consequence the pulse generated by an α-decay occurring *inside* the detector corresponds to the total transition energy (α-particle plus recoil), unlike those generated by α-particles incoming from outside. This allows to discriminate unambiguously between internal and external contamination.

Due to its large atomic number, acceptable mechanical properties and reasonable cost, lead is often used as shielding material and many measurements have been carried out on its intrinsic radioactivity [13–18]. The main contaminant in commercial lead is normally ^{210}Pb along with its daughter nuclides ^{210}Bi and ^{210}Po. Due to the relatively long lifetime of ^{210}Pb (22.3 yr) the abundance of these nuclides in lead can be much larger than expected from secular equilibrium: it is, however, much reduced in old lead. The very soft beta (E_{max} of 16.5 and 63 keV) and gamma (46.5 keV) rays of ^{210}Pb are normally self-absorbed. On the contrary the energetic electrons ($E_{max} = 1.16$ MeV) from ^{210}Bi can be revealed by bremsstrahlung and characteristic X-rays in lead. The only detectable gamma activity is due to the 803.2 keV γ-ray emitted in the decay of ^{210}Po into ^{206}Pb, but its branching ratio is only 0.001%. ^{210}Po can be revealed also by its monochromatic 5.304 α-particle. A company (Johnson and Matthey) succeeded [17] in producing expensive lead to be used in the electronics industries with an activity lower by more than two orders of magnitude with respect to normal commercial samples. Old lead, where ^{210}Pb has substantially decayed, represents an alternative, and so far less expensive, solution.

Standard techniques were used in a previous experiment to determine radioactive contaminations in a lead ingot from the load carried by a roman ship sunk near Sardinia [18] and to compare them with those of samples of electrolytic "modern" and of specially prepared Johnson and Matthey lead [19,20]. Contaminations of 150 to 200 Bq kg^{-1} due to ^{210}Po were found in modern lead from measurements on X-ray lines and bremsstrahlung and with gamma and alpha spectroscopy. No such activities were found in Johnson and Matthey and Roman lead with upper limits of about 1 Bq kg^{-1}.

We report here improved results obtained on samples of the above mentioned materials with the thermal method [21].

2. Experimental approach

Various difficulties are expected in the use of the thermal method to determine radioactive contaminations in lead:

a) The Debye temperature of lead is low (about 82 K [22]).

b) Lead is a superconductor. The contribution of the conduction electrons to the heat capacity is negligible if the bolometer is kept well below the transition temperature, but a considerable portion of the energy of the incoming particle is spent in breaking the Cooper pairs which could not recombine within the time scale of thermal pulses. It has been pointed out however [23] that in materials with low Debye energy and high critical temperature the quasiparticle recombination rate should exceed the pair-breaking rate with a consequent acceptable thermalization. In fact, superconductors have already been successfully operated as absorbers in bolometers with superconductor phase transition [24] and thermistor thermometers [25,26]. Absorbers made of Sn and Bi with neutron transmutation doped (NTD) thermistors are studied to search for the 17 keV neutrino [27]. A systematic investigation on various superconductors carried out by the Genoa group [28] indicates that the thermalization efficiency of the energy deposited in the bolometer by the incoming particle is a universal function of the ratio T/T_D. This efficiency is near to one for $T/T_D > 3 \times 10^4$, but decreases rapidly below this value. Due to their low Debye temperature, lead bolometers [29] should therefore operate successfully down to a few tens of millikelvin, unlike superconductors of higher T_D. A very small (about 1 mm^3) monocrystal of lead was in fact used as a bolometer recently [28], but operation of larger lead detectors is expected to be quite harder.

c) Crystallisation is expected to clean the material from most contaminants including the radioactive ones. The measured activity of crystallised samples could therefore be lower than the original one.

Despite these difficulties, which indeed were present and hindered our measurements, we were able to operate a few detectors made out of lead and to determine the radioactive contaminations of various samples of this material.

All measurements were carried out at temperatures of a few tens of millikelvin in a dilution refrigerator operating in Milan. The thermal pulses were measured by means of a NTD thermistor developed by the group of Haller [30], kept in thermal contact by means of nonconductive epoxy. The thermistor was biased at the best operating conditions using a load resistor and a battery. As the impedance of the sensor was low (table 1, the relatively high parasitic capacitance of the wires from the detector to outside was tolerable. Therefore the signal was read out with a differential low-noise preamplifier operated at room temperature and used also for the characterization of the thermistor. The circuit was a DC coupled version of our previous differential "warm" version [31].

All detectors made with the various lead samples were calibrated with a ^{232}Th source placed outside the refrigerator. The heat capacity extracted from the ther-

mal pulses was found to be always compatible within a factor of 5 at the maximum with respect to the value calculated on the basis of the presently known Debye temperature [22]. The counting rate, when exposing the lead samples to known radioactive sources, was always in agreement with the expected value, thus assuring that the entire sample was indeed active.

We would finally like to stress that the background of cosmic rays was a serious problem in these measurements: unfortunately this experiment had to be carried out in Milan since our dilution refrigerators in the Gran Sasso were dedicated to double beta decay experiments [7,12]. Better sensitivity to radioactive contaminations could be achieved by operating lead bolometers, as well as all other detectors, underground.

3. Results

We report here the results of measurements performed with five thermal detectors made with samples of modern, low activity and old lead.

3.1. Modern lead

A 100 g crystal of modern electrolytic lead previously analysed with standard γ spectroscopy and found free from γ radioactivity was grown and a 4.7 g sample was cut from its interior. The base temperature and resistance of the thermistor glued to it are reported in table 1 together with the optimum operating conditions achieved by applying a bias of 4.3 mV through a 1.2 GΩ load resistor. In the spectrum of the pulses at low energy the main peak was due to the 1.461 MeV line of environmental ^{40}K. The spectrum in the high energy region, shown by the solid curve of fig. 1, indicates the presence of the 5.4 MeV α line due to ^{210}Po with a full width half maximum (FWHM) resolution of $\sim 7\%$. The contamination of ^{210}Pb is 16.4 ± 1.8 Bq kg^{-1} (one σ), a value lower by almost an order of magnitude with respect to that obtained on the same type of lead in our previous experiment with standard techniques. We

believe that this reduction of the radioactivity is a consequence of the "cleaning" by the crystallisation.

In order to prove this effect, which would prevent the thermal detection of the actual contamination of lead, we have carried out a second measurement with a 4 g sample simply cut from an ingot of the same lead. In the operating conditions reported in table 1 this bolometer yielded similar and in fact somewhat better performance than the crystalline one. This surprising result is probably due to the polycrystalline structure of the second sample. It has in fact been shown for other superconductors [28] that monocrystallisation is not required to obtain good bolometric performances. The spectrum, shown by the dotted curve of fig. 1, indicates a ^{210}Po peak (4% FWHM) corresponding to a contamination of 142 ± 22 Bq kg^{-1} (one σ) definitely larger than for the crystalline lead.

A similar result and similar resolution (6% FWHM) is obtained with a 5 g sample of *melted* modern electrolytic lead operated as reported in the table. The ^{210}Po contamination is found to be 116 ± 1 Bq kg^{-1} (one σ) (see the dashed curve of fig. 1). This figure is in reasonable agreement with that obtained with the previous sample. The contaminations found in polycrystalline and melted lead are consistent with those obtained with standard α and γ spectroscopy, while crystallisation improves the purity by about an order of magnitude. Since this last process is quite simple in lead, due to its low melting point, it could be usefully employed to produce low radioactivity shielding materials.

3.2. Special low activity lead

A 11.9 g sample of lead was cut from an ingot of the special low radioactivity material of Johnson and Matthey [18] and operated under the conditions reported in table 1. In addition to the peaks at 1461 and 2615 due to ^{40}K and ^{208}Tl, respectively, a small α activity due to ^{210}Po (4% FWHM) can be seen (fig. 2). It corresponds to a contamination of 0.14 ± 0.03 Bq kg^{-1} (one σ), three orders of magnitude less than

Table 1
Base and operating parameters of the different lead bolometers: m is the mass of the lead sample, R_L is the load resistance, V the bias on the thermistor, R_{base} and R_{op} are the thermistor resistances at the base and operating temperatures T_{base} and T_{op}. The radioactive contamination A is also reported

	m [g]	R_L [GΩ]	V [mV]	T_{base} [mK]	R_{base} [MΩ]	T_{op} [mK]	R_{op} [MΩ]	A [Bq/kg]
Modern (crystal)	4.7	1.2	4.3	20	4	24	1	16.4 ± 1.8
(cut)	4.0	1	4.0	21	1.4	25	0.6	142 ± 22
(melt)	5.0	0.2	2.6	30	1.6	38	0.7	116 ± 11
Johnson, Matthey (cut)	11.9	1	9.6	13	16	16	13	0.14 ± 0.03
Roman (melt)	8.6	0.2	3.1	23	1	27	0.6	< 0.02
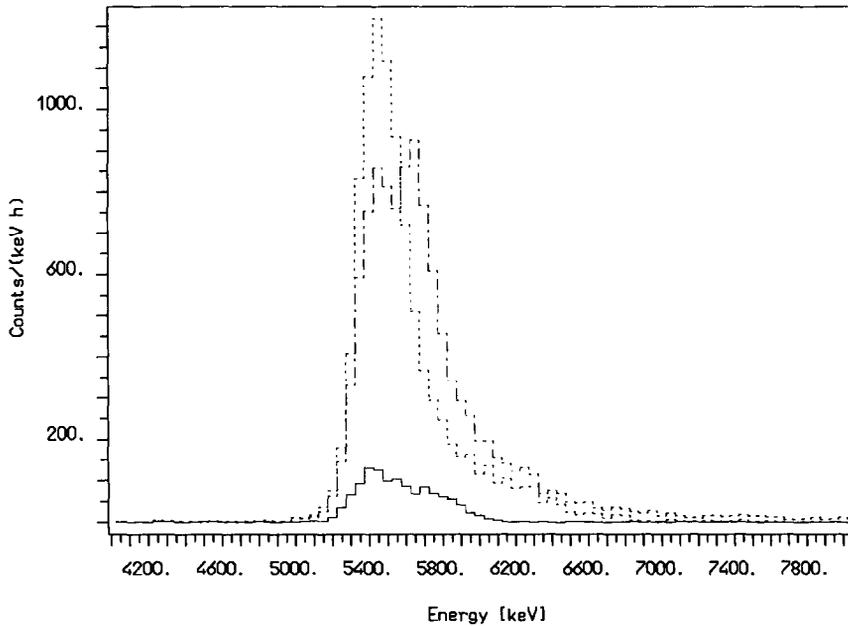
Fig. 1. The upper part of the spectra obtained with modern lead: crystallised (full line), amorphous (dotted) and melted (dashed). The assymetry in the peaks is typical of these superconductor detectors.

in modern lead. It is lower than the upper limits obtained in our previous experiment [19,20] using conventional detection methods. In order to test this measurement of such a low contamination we have anal-

ysed a background spectrum obtained in the Gran Sasso Underground Laboratory with a 400 cm^3 intrinsic germanium detector heavily shielded against environmental radioactivity. This germanium diode is
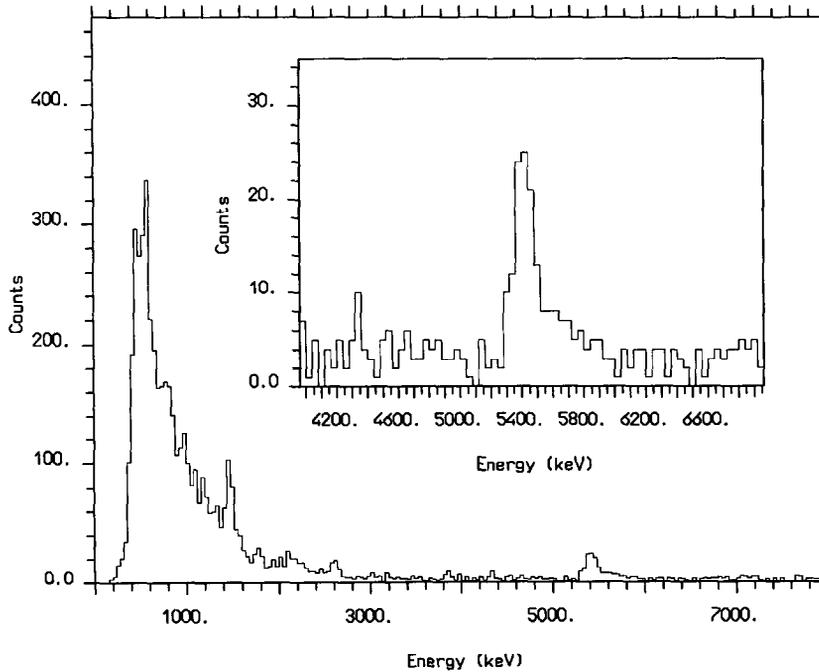
Fig. 2. The upper part of the spectrum obtained with special low radioactivity lead. In the inset the [210]Po region.

shielded from the cooling system by a three mm thick plate of Johnson and Matthey lead placed *inside* the detector cup. This peculiar property of the setup allows to detect the 46.5 keV γ-rays which would have been absorbed by the cup if the lead had been placed outside. The peak due to ^{210}Po (FWHM of 4%) is found to be 0.26 ± 0.03 Bq kg^{-1}, where the error is mainly systematic and due to the difficulty to evaluate the efficiency of the detector to this internal radioactive source. This figure is in reasonable agreement with the result of the thermal measurement if one considers that the two samples of lead were not the same.

3.3. Roman lead

The sample of Roman lead was melt from the bulk of the same ingot previously analyzed with standard techniques. The mass was 8.6 g and the base and operating parameters are listed in the table. In the spectrum reported in fig. 3 no evidence appears for the α peak due to ^{210}Po where the resolution is expected to be the same as for the previous measurement, while background peaks due to ^{40}K and ^{208}Tl are clearly present. The corresponding upper limit of the contamination or ^{210}Pb is 0.02 Bq kg^{-1} at the 90% confidence level.

4. Conclusions

From the results of the present experiment we can conclude that:

a) the thermal technique provides an excellent method to determine the initial ^{210}Po content in lead;

b) a simple crystallisation reduces this contamination by about an order of magnitude;

c) a contamination of a few tenths of a becquerel per kilogram due to ^{210}Pb is still present in modern lead specially produced to achieve low radioactivity. This contamination is, however, lower by about three orders of magnitude than in commercial low radioactivity lead;

d) no ^{210}Pb is found in Roman lead with an upper limit of about two centibecquerel per kilogram.

We conclude that the thermal detection technique is very promising to search for low radioactive contaminations. It shows that at present the best available lead for low level shielding is the Roman one, but that modern lead can be efficiently cleaned by crystallisation at least for those contaminants which are not chemically compatible with lead.

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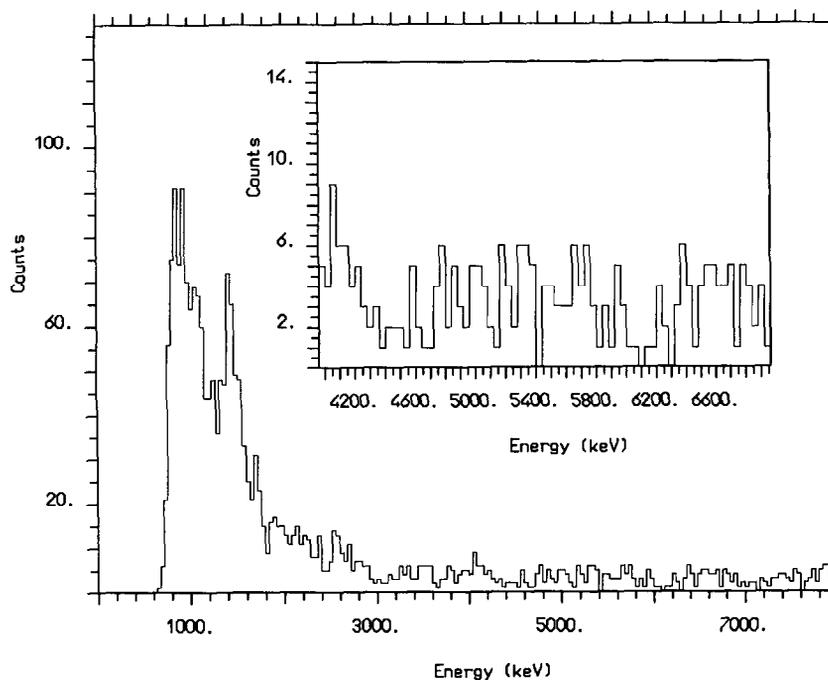
Fig. 3. The upper part of the spectrum obtained with Roman lead. In the inset the ^{210}Po region.

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