Evidence for superconductivity onset at 40 K in a carbon-based system

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Evidence is presented for the probable occurrence of superconductivity in the Y–Al–C system, with a resistivity onset close at 40 K. The samples have been prepared using a novel synthesis route.

THE importance of carbon in a materials world is just beginning to be appreciated with the discovery not only of the fullerides, but also of nano tubules and novel encapsulation chemistry[1,2]. The exotic behaviour of fullerides, tubules and capsules is to be contrasted with the seemingly inelegant synthesis techniques (employing basically random-access methods of the brute-force arc furnace or high-temperatures) as distinct from the several elegant sequential methods of the classical synthetic organic chemist. We have nevertheless used the former liberating procedure to search for new routes for the discovery of novel materials hoping that the end would justify the means.

Recently, quarternary systems[3-6] such as those derived from Y–(Pd,Ni)–B–C have been considered to be alternative routes for the synthesis of high-temperature superconductors in a numerological approach. Compounds such as YNi_2B_2C are derived from the $ThCr_2Si_2$ structure with YC layers and Ni_2B_2 layers. We sought to examine the consequence of replacing the nominally trivalent B by tetravalent carbon, replacing at the same time the nominally trivalent Al for the bivalent Ni. We report in this communication, evidence for high T_c in a ternary carbon-based system involving metal atoms which are conventionally not associated with magnetic properties.

These results have been obtained as a consequence of a novel, as yet unpublished, low-temperature route for the synthesis of metal–carbon compounds[7]. In our synthetic methods, high-temperature polymers are used as starting material for the source of carbon and other reactive elements. Basically, the scheme visualizes a wrapping of the reactant metal salt by the polymer before reaction/graphitization so as to encapsulate the product in a graphitic matrix, thereby rendering stability to the product against corrosive attack in the ambient atmosphere[8]. The general scheme is schematically written as follows:

$$C_l H_m X_n^v + MY_p^w \xrightarrow{\text{inert gas}} qH_w Y + rH_v X + C_{l'} X_s Y_t H_{m'} + MY_{p-q-t} X_{n-r-s} \cdot C_{l-l'} H_{m-qw-rv-m'} \quad (1)$$

$$MY_{p-q-t} X_{n-r-s} \cdot C_{l-l'} H_{m-qw-rv-m'} \xrightarrow{\text{hydrogen}} M \cdot C_z + \text{other products.} \quad (2)$$

where M is a metal ion such as Y, Al, Mo, W, Ti, Cd, Ni, Co, Fe, Mn, etc. X and Y are electronegative elements such as the chalcogenides or halides. The final $M \cdot C_z$ product in equation (2) could be composite of a metal or metal carbide dispersed in a graphitic matrix. We have already achieved fair amount of success by this method for making novel carbon-based materials useful for rechargeable lithium-based batteries[9] with high current densities (> 65 Whr/kg), for stabilizing nano particles (< 20 nm diameter) of various oxides, sulphides or metallic elements or alloys that could find several applications in various areas including catalysis.

The Y–Al–Ni–C compositions were attempted to be synthesized according to schemes (1) and (2). The actual details of the procedure will be given elsewhere. The Y–Al–Ni–C systems did not show any evidence for the formation of phases reported earlier[4,5]. Chemical analyses of the Y–Al–C systems show the Y : Al ratio to be close to the starting composition with negligibly small amounts of oxygen. X-ray photoelectron spectroscopic studies on these samples show the carbon to be predominantly in the carbide form. However, there is also a large amount of oxygen presumably as a surface adsorbed species. Two species of Y and Al are found with the predominant species having a binding energy close to that of the element in its metallic state. Cl [used as X in equation (1)] and S [Y of equation (2)] were found only in trace amounts. The mixture is pelletized and heated at 800°C in hydrogen to yield a strong stable pellet with few cracks. These pellets do not regain their mechanical strength after grinding, pelletizing and re-sintering. The as-heated pellets were used for the measurements. So far the best X-ray diffraction pattern has been obtained with the composition in which the Y : Al ratio is 1 : 2. Most of the X-ray diffraction peaks in the AlY_2C_x composition may be indexed on the basis of a starting tetragonal unit cell with $a \approx 3.34$ Å and $c \approx 9.85$ Å. These parameters are similar to those of $LuNi_2B_2C$ system[4]. Pure Y–C or Al–C composition could not be made as a pellet suitable for measurement.

The first experiment with a product which had the nominal composition of YNi_2AlC_4 had a large amount of elemental nickel so that the sample was mainly ferromagnetic. The electrical resistance of this sample showed a maximum at ~ 30 K (Figure 1). An anomaly in the *ac* magnetic susceptibility was noted at this temperature. This behaviour was reproducible over several heating and cooling cycles in a subsequent batch with the same composition. Experiments on Y–Al–C systems in which Ni is completely absent were eventually performed. The best results as far as superconductivity

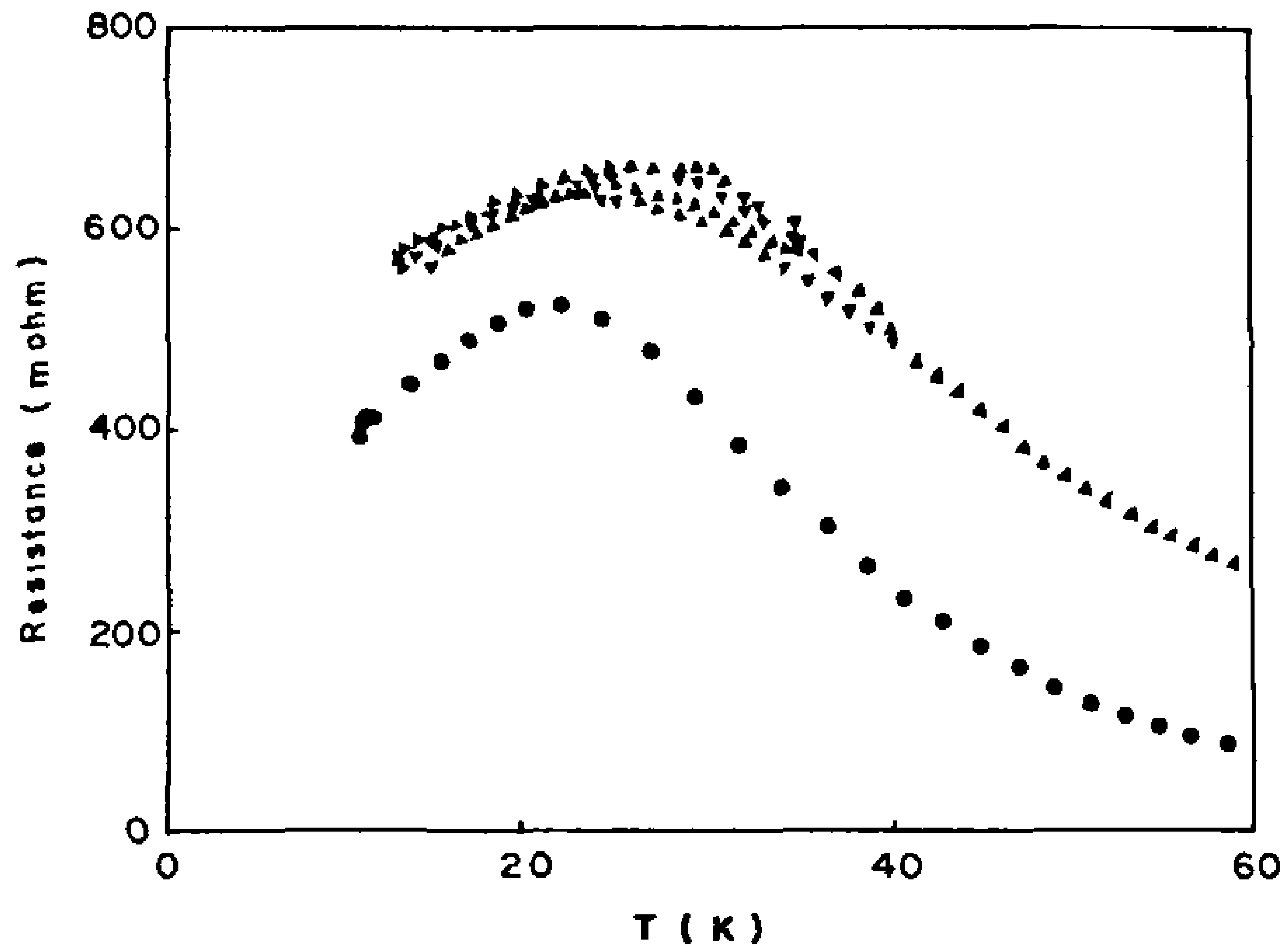

Figure 1. Plot of electrical resistance versus temperature of the as-prepared pellet with the nominal composition YNi_2AlC_2 (filled circles) and YNi_2AlC_4 (triangles) The reproducible cycling at low temperatures is shown for the latter.

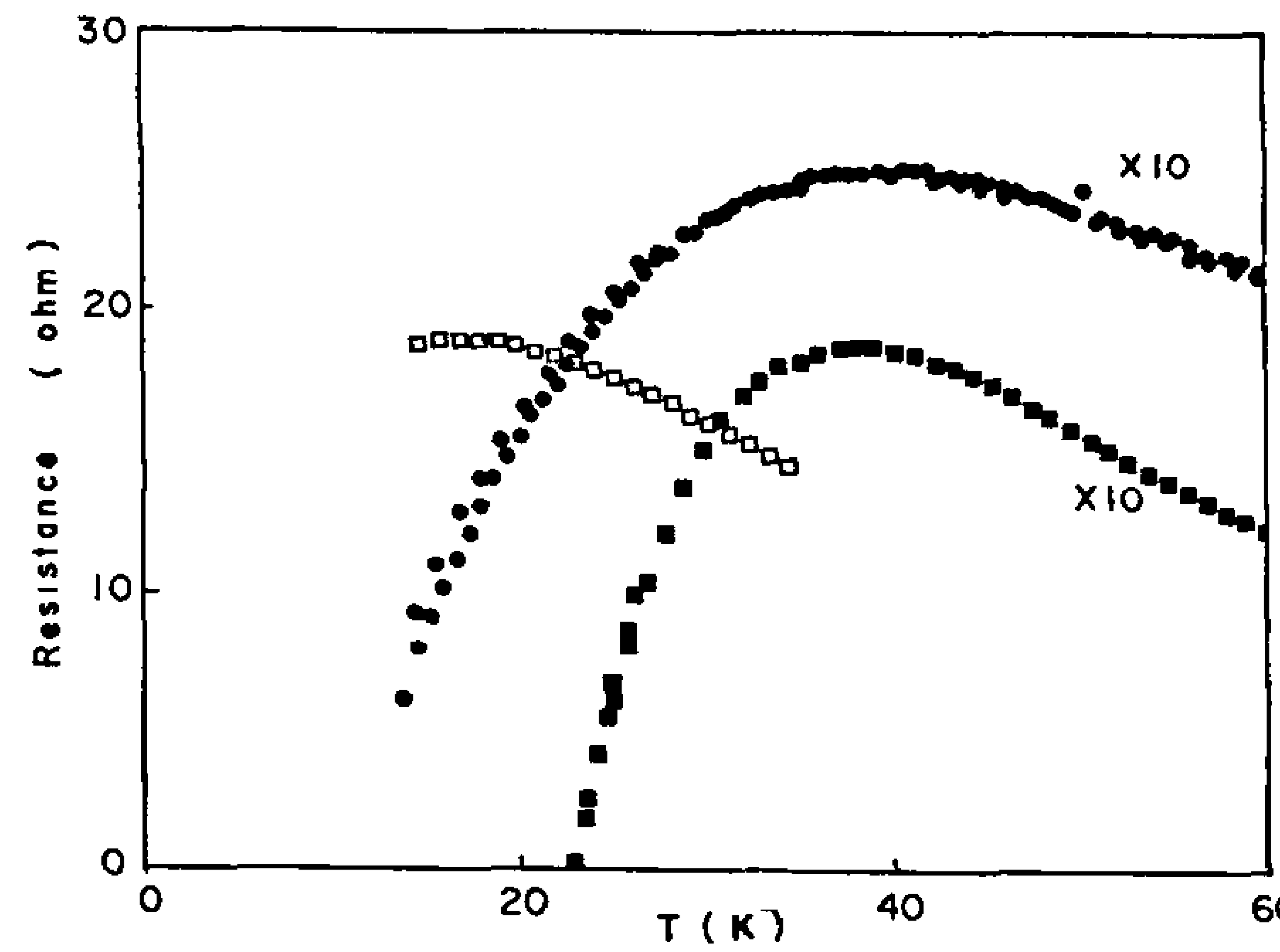

Figure 2. Plot of electrical resistance of the as-heated pellets of various nominal Y–Al–C compositions; filled squares: $YAlC_6$; filled circles: $YAlC_4$; open squares: AlY_2C_4.

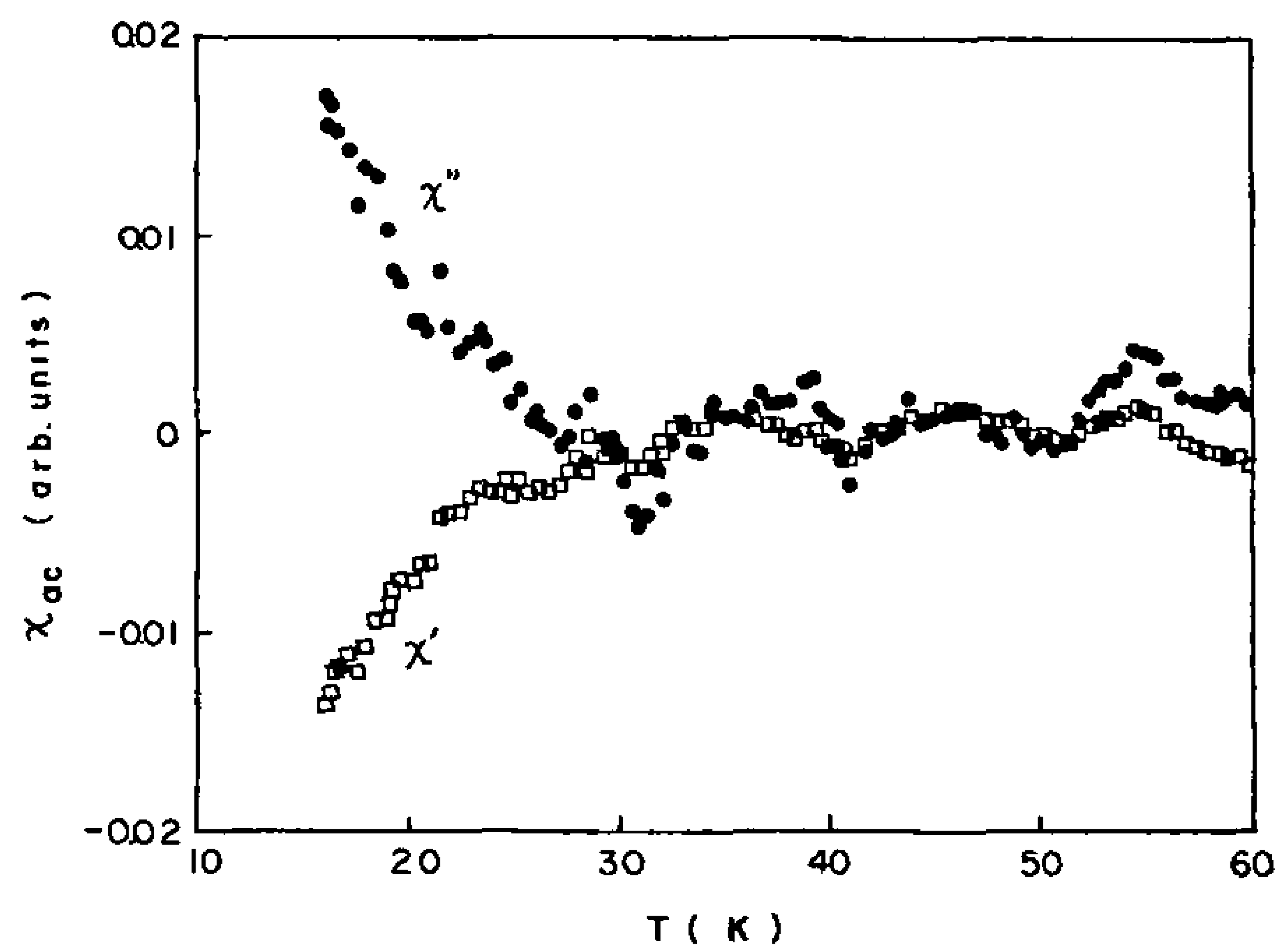

Figure 3. Plot of *ac* susceptibility (amplitude: 10 Oe; frequency 27.1 Hz) of the $YAlC_6$ composition with zero resistance (see Figure 2). The in-phase (X') and out-of-phase (X'') values of the susceptibility are referred to that of a standard Gd_2O_3 sample.

is concerned are obtained in the compositions in which the Y : Al ratio is 1 : 1. Thus the nominal composition $YAlC_6$ gave a T_c onset at 40 K and a zero resistance at 24 K with the zero resistance being reproduced during the heating–cooling cycle in one portion of the pellet (Figure 2). All portions of the pellet show a nonlinear behaviour of the electrical resistance below 48 K. The zero resistance of the $YAlC_6$ composition is obtained over several cycles of heating and cooling. Similarly, a nominally $YAlC_3$ composition yielded an onset at the same temperature with the extrapolated value of the temperature at which zero resistance could be obtained being between 10 and 15 K.

The *ac* magnetic susceptibility on a powdered part of the same batch showed a reproducible anomaly in four measurements which commences at 40 K. The average susceptibility from these measurements is shown in Figure 3. The anomaly seen is clearly within experimental errors. The magnitude of the anomaly is small, suggesting that the superconducting fraction is small. We are not able to comment on the inter-grain and intra-grain contributions as yet. The rate of change of the susceptibility is prominent below the temperature at which the zero resistance has been obtained (Figure 2).

From a phenomenological point of view, our results are important not only because of evidence for demonstrating the possible existence of T_c in a novel system but also demonstrating the possibility of a T_c comparable to that of the first cuprate, $La_{2-x}Sr_xCuO_4$, in the Bednorz–Muller era. A T_c close to 40 K has not been achieved in any system other than these cuprates. The importance of a layered structure either in the graphite-like composite structure or in the Y–Al–carbide structure systems is considered to be an important ingredient. Superconductivity between 6 and 12 K in Y–C systems has been reported earlier[10]. We suggest the possibility that this value may be increased further to as yet unanticipated temperatures.

It is not clear as yet whether a complex crystal structure[3] in such quarternary compounds is a necessary prerequisite for enhancing T_c. At the same time there may be features associated with carbon chemistry that are relevant to high T_c. The establishment of high T_c (greater than BCS limit) in a carbon-based compound is important because of its symmetric location between the inert gas atoms in the 2nd row of the periodic table. The question of hole-pairing that has been proposed for the oxide may not be important.

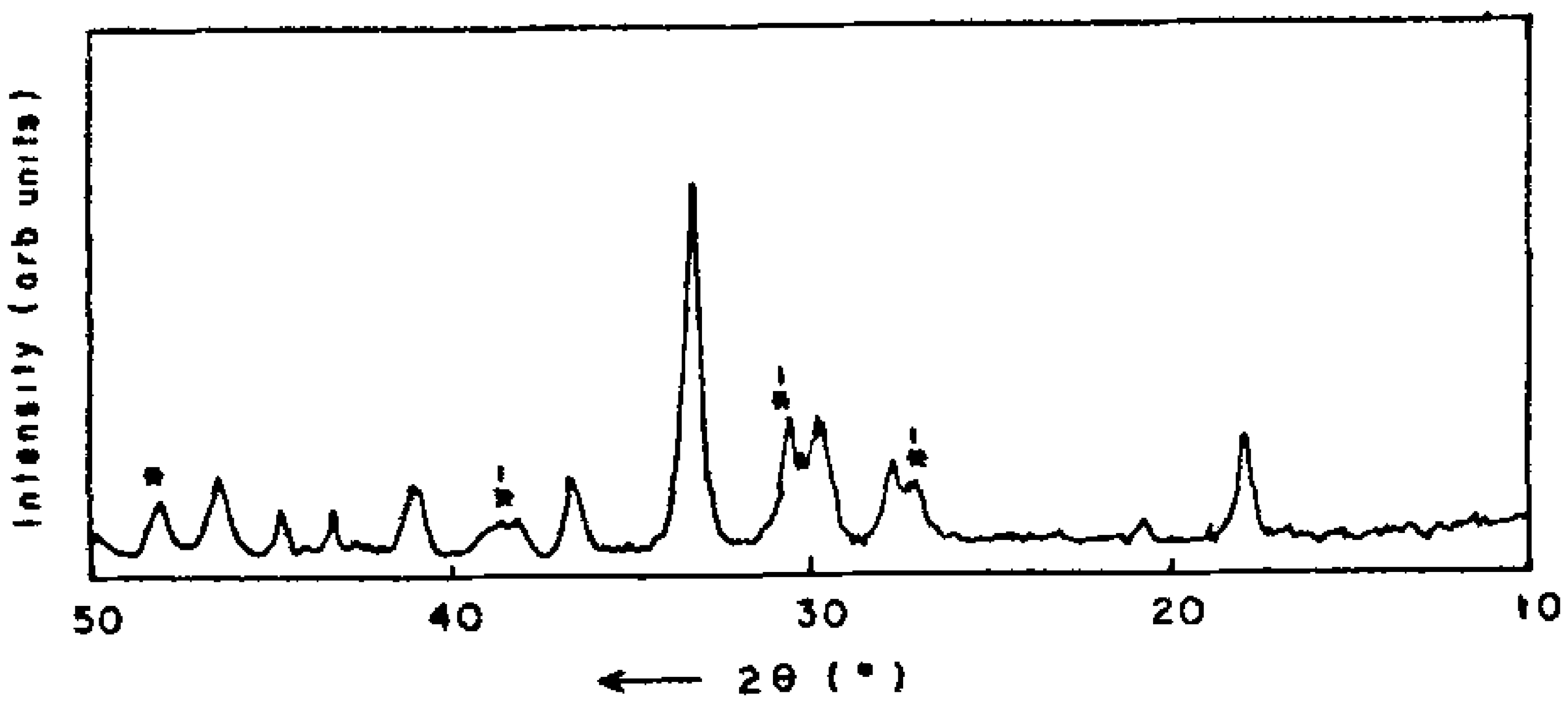

Figure 4. X-ray diffraction pattern from the composition in which the Y : Al composition is 2 : 1. The stars correspond to patterns obtained when Al is absent.

Quite strictly, our results establish the possibility of high T_c in an Y–Al–C–O–Cl–S with the likely possibility of it being present only in the Y–Al–C system. All the compositions which are superconducting have the X-ray diffraction peak close to $2\theta = 33°$, which is prominently seen in compositions with Y : Al being close to 1 : 2 (see Figure 4). However, the resistance anomaly in this sample (Figure 2, seen in all parts) is not only weak but occurs at a lower temperature. This indicates that there is a critical Y : Al composition for high T_c. However, the existence of some other carbon-containing compound which shows high T_c cannot be ruled out. Electron microscopy studies on the Y : Al = 1 : 1 compositions so far show a predominant deposition that is amorphous plate-like on the grid encapsulating nano particles of diameter less than 10 nm. Further analysis is underway.

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