

technical memorandum

Daresbury Laboratory

DL/SCI/TM97E

**COMBINING X-RAY ABSORPTION SPECTROSCOPY AND DIFFERENTIAL SCANNING CALORIMETRY:
A POTENTIAL TECHNIQUE FOR INTER-RELATING THE KINETICS AND ENERGIES OF PHASE
TRANSFORMATIONS IN LUBE OILS WITH CHANGES TO THE LOCAL ATOMIC STRUCTURE OF
THE CONSTITUENT MOLECULAR COMPONENTS**

by

**K. J. ROBERTS, University of Strathclyde & SERC Daresbury Laboratory; and
D. ADAMS, Exxon Chemical Ltd., Abingdon, Oxon.**

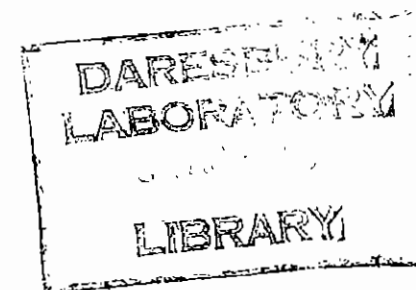
AUGUST, 1993

G93/760

Science and Engineering Research Council

DARESBUY LABORATORY

Daresbury, Warrington WA4 4AD



CCLRC LIBRARY & INFO SERVICES



C1005823

LENDING COPY

© SCIENCE AND ENGINEERING RESEARCH COUNCIL 1993

Enquiries about copyright and reproduction should be addressed to:—
The Librarian, Daresbury Laboratory, Daresbury, Warrington,
WA4 4AD.

ISSN 0144-5677

IMPORTANT

The SERC does not accept any responsibility for loss or damage arising from the use of information contained in any of its reports or in any communication about its tests or investigations.

Combining X-ray Absorption Spectroscopy and Differential Scanning Calorimetry: A Potential Technique for Inter-relating the Kinetics and Energetics of Phase Transformations in Lube Oils with Changes to the Local Atomic Structure of the Constituent Molecular Components.

K. J. Roberts

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK and SERC Daresbury Laboratory, Warrington WA4 4AD, UK.

D. Adams

Exxon Chemical Ltd., Abingdon, Oxon OX13 6BB, UK.

Technical Memorandum based on a paper presented to the Workshop on Simultaneous WAX/SAS/DSC Techniques, Daresbury Laboratory, 22/5/92.

The oxidation of lubricant oil inside engines (figure 1(a)) is a major problem facing oil and lubricant additive companies. Failure to control this oxidation leads to an increase in the viscosity of the oil, resulting in a reduction in lubricant efficiency (figure 1(b)). This in turn may cause sludge formation and an increase in wear of the engine parts, decreasing fuel efficiency and increasing exhaust emissions. The ability to inhibit this oxidation is therefore a key requirement for new lubricants. This oxidation is known to be catalysed by iron dissolved in the oil as a result of corrosion of engine parts. It is known that certain transition metal compounds, such as ZDDP's and copper salts, act as oxidation inhibitors, as well as organic radical traps for hindered phenols and aromatic amines. Although lubricant oxidation inhibitors have been known for many years, the detailed mechanism by which they exhibit this action has not been studied.

The effects of additive action on the anti-oxidation performance of oil formulations is traditionally assessed with the aid of the technique of differential scanning calorimetry (DSC). DSC traces are recorded as a function of temperature and reveal the difference, in terms of heat input, between an inert reference compound and the sample under investigation that is needed if both sample and reference are to be maintained at the same temperature. As such the technique records the enthalpy change associated with any phase transformations that take place within the material. In lube oils it is used to reveal the temperatures associated with the thermal degradation of the product. Figure 2 shows two DSC traces demonstrating how the presence of particulate Fe within the formulation results in an acceleration in the breakdown of lube oil. However given the variety of metal ion species likely to be present in the lube formulation the REDOX processes associated with the oil degradation are not clear.

Using a combination of XAS and DSC provides a potential solution to this problem with the former technique revealing changes to oxidation states of the various species associated with the energetics of the process revealed by the latter technique. Benchmark tests carried out by Edwards et al in 1990 [1] have demonstrated that high quality XAS spectra can be obtained in a matter of seconds using the quick-scanning or QEXAFS technique. QEXAFS uses a continuous scan of the monochromator axis and time integration of the data rather than the more conventional step/count approach. QEXAFS spectra were taken dynamically of a sample of nickel

formate dihydrate (NF) over the temperature range 25°-320°C. A DSC scan taken of the sample (figure 3(a)) reveals three noticeable features at temperatures of 170°C, 210°C and 270°C which can be ascribed to transitions from the hydrated to anhydrous formate (A), from anhydrous formate to oxide (B) and from oxide to metal (C). The reduction of white line intensity in the sample associated with transition C can be seen clearly (figure 3(b)) from the XANES data which was recorded with an acquisition time of 4 s as a function of temperature. The reaction to the metallic state progresses by a nucleation and growth mechanism as evidenced from the isothermal (T = 257°C) Fourier transformed EXAFS data (figure 3(c)), recorded at 40s/spectra scan, taken in the meta-stable region close to transition C.

These benchmark experiments demonstrate the feasibility of the XDSC approach. Significant improvements can be expected in data acquisition by using the greater photon flux available on Wiggler beamline 9.3 as well as through improvement in data acquisition software. Thus the collection of the near-edge XANES spectra in time periods less than 500 ms should be easily realisable.

Extension of the technique to examination of the kind of dilute analytes present in lube oils is also feasible (figure 3(d)) as the fluorescence mode of XAS easily has the sensitivity (figure 4) to detect the trace elemental concentrations present in the additives mediated oil. For this the near edge K-edge spectra of the expected Zn, Fe and Cu atoms are all highly distinctive (figures 5-7) and thus the monitoring of the oxidation states of all three elements during a DSC scan is quite feasible. A schematic for a combined DSC/XAS cell is given in figure 8.

Acknowledgements

One of us (KJR) gratefully acknowledges SERC for the financial support of a Senior Fellowship. Additional thanks are due to Hal Shaum (Exxon Corporate Research, Clinton, NJ, USA) who provided the Lube Oil DSC data and various co-workers, referenced in cited publications, for the XAS data.

References

- 1 Quick Scanning EXAFS - A Structural Probe for Investigation of Chemical Reactivity in the Solid-State, B. Edwards, C. D. Garner and K. J. Roberts, Proceedings of the 2nd European Conference on Progress in X-ray Synchrotron Radiation Research (Eds. A. Balerna, E. Bernieri and S. Mobilio), Società Italiane di Fisica, Conference Proceedings 25 (1990) 415-419
- 2 X-ray Absorption Spectroscopy Studies of the ZDDP/mild steel interface, E Ferrari, K J Roberts, A Dent and D Adams, work in progress 1993.
- 3 An Investigation of the Local Structure around Iron in VC-VDC Polymer Coating on Mild Steel using Glancing X-ray Absorption Spectroscopy, S. Pizzini, K. J. Roberts, I. Dring, P. J. Moreland, R. J. Oldman and J. Robinson, J. Materials Chemistry 2 (1992) 49-55
- 4 Application of Glancing Angle Absorption Spectroscopy to the Investigation of the Surfaces of Cu Thin Films, S. Pizzini, K. J. Roberts, I. S. Dring, R. J. Oldman and G. N. Greaves, Physica B. 158 (1989) 676-678
- 5 Fluorescence EXAFS Studies of Cu-rich Precipitates in Iron Alloys in Relation to their Role in Embrittlement Processes, S. Pizzini, K. J. Roberts, W. Phythian and C. English, publication in preparation, 1993

Figure Captions

Figure 1. Schematic showing the effect of lube oil oxidation on product performance; (a) the role of Fe particulates in the oxidation process; (b) the effect of Cu containing additives in reducing the oxidation related increase in lube oil viscosity.

Figure 2. DSC scans as a function of heating time (heating rate 1°/minute from 100°C) for an oil formulation without (a) and with (b) the presence of catalysing Fe particulates.

Figure 3. Quick scanning XAS investigation of the decomposition of NF, after [1]; (a) DSC scan of NF showing the principle regions of thermally-induced structural change; (b) quick-scanned XANES data, recorded *in-situ*, of NF at the Ni K-edge recorded between 250°C and 300°C with a data acquisition time = 4 s, showing the thermally-induced reduction of NiO to metallic Ni at around 265°C; (c) Fourier transformed QEXAFS data (100 ms integration time and monochromator scan speed 20 mdeg s⁻¹) and isothermally in the meta-stable region close to C (figure 3(a)) showing the slow thermal reduction of NiO to metallic Ni.

Figure 4. X-ray fluorescence emission from an Fe/1.5%Cu/1.5%Ni alloy excited at three X-ray energies; (a) 8.16KeV (just above the Fe K Edge); (b) 8.4 KeV (just above the Ni K edge); (c) 9.09 KeV (just above the Cu K edge) showing the clear resolution of the fluorescence spectra of these three analytes, after [5].

Figure 5. XAS near-edge spectra at the Zn K edge: (a) neutral ZDDP; (b) Zn²⁺S; (c) Zn⁰ metal; showing the clear resolution of edge structure as function of oxidation state.

Figure 6. XAS near-edge spectra at the Fe K edge: (a) Fe⁰ metal; (b) Fe²⁺Fe₂³⁺O₄; (c) Fe²⁺O, (d) Fe₂³⁺O₃.

Figure 7. XAS near-edge spectra at the Cu K edge: (a) Cu²⁺O; (b) Cu₂O and (c) Cu⁰ metal.

Figure 8. Schematic representation for an instrument for the simultaneous acquisition of XAS and DSC data: the set-up is shown in the 45° fluorescence geometry.

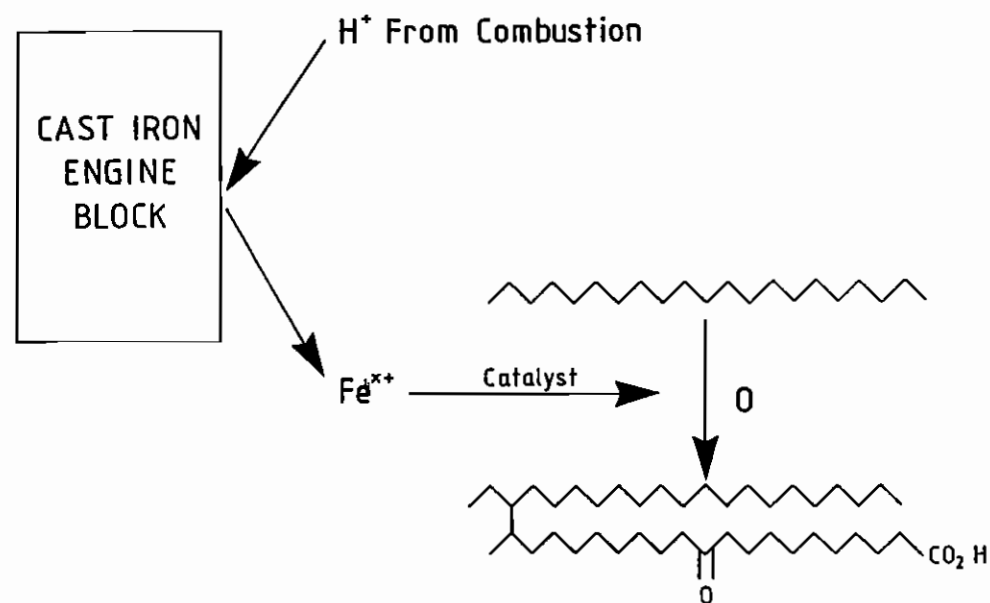


Fig.1 (a)

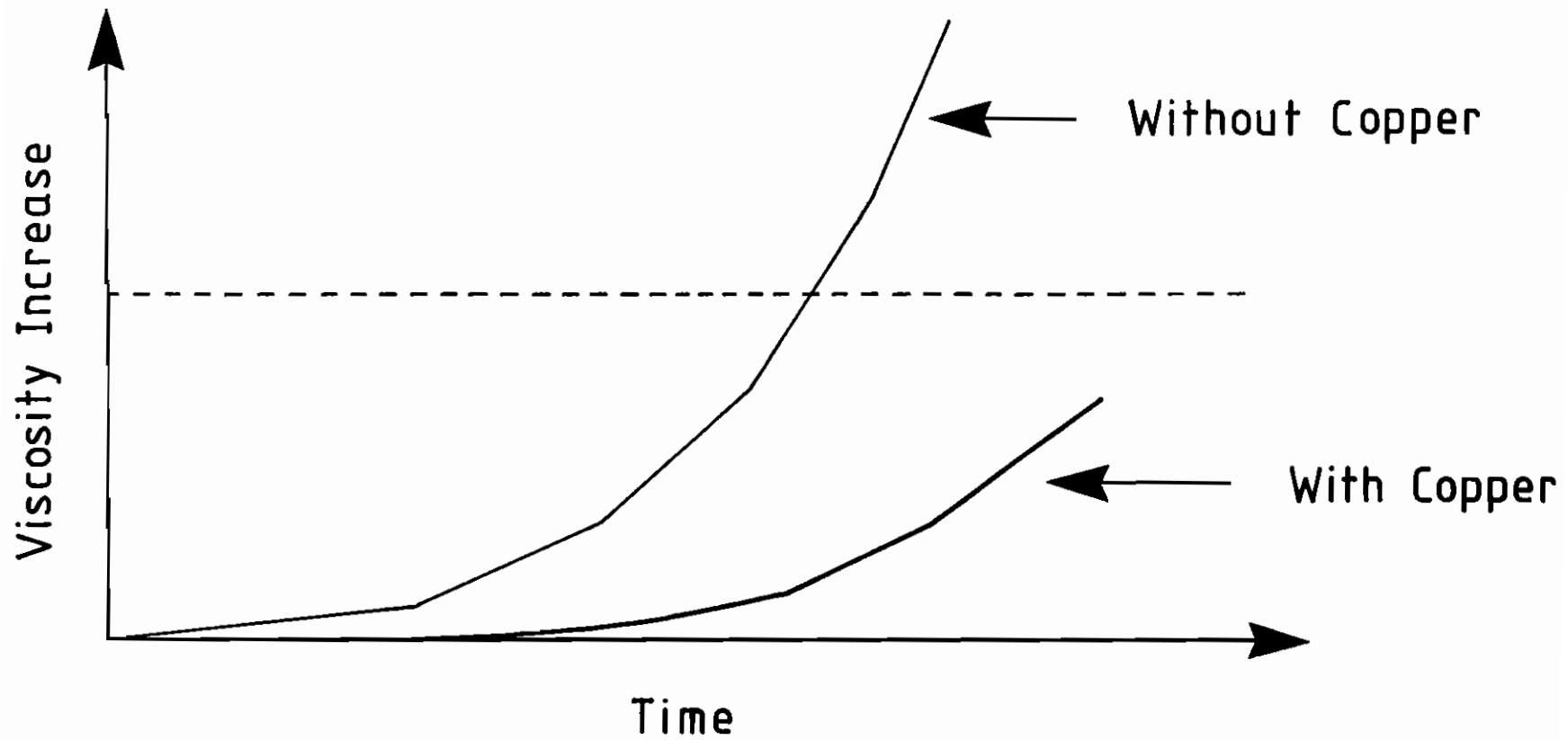


Fig.1 (b)

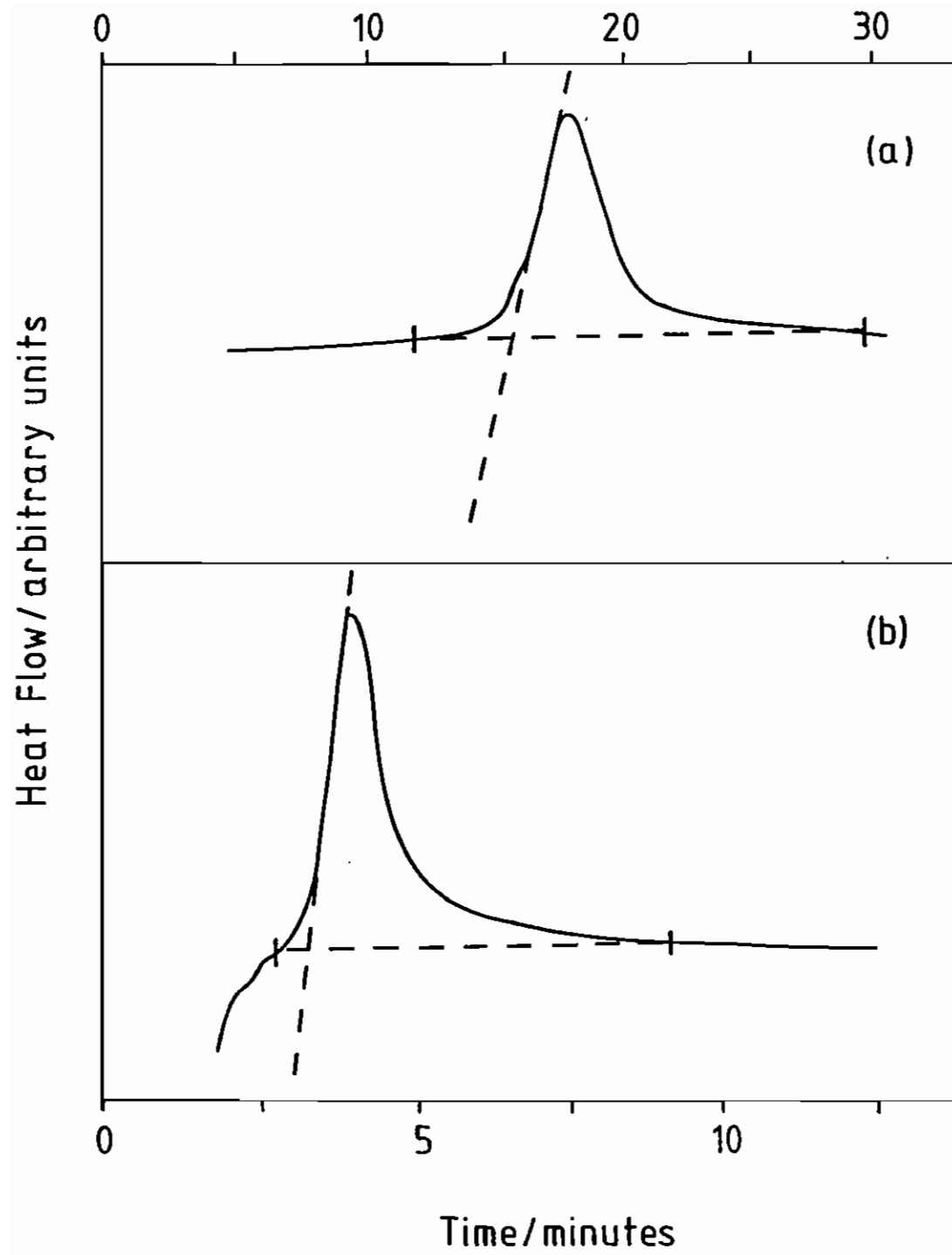


Fig. 2

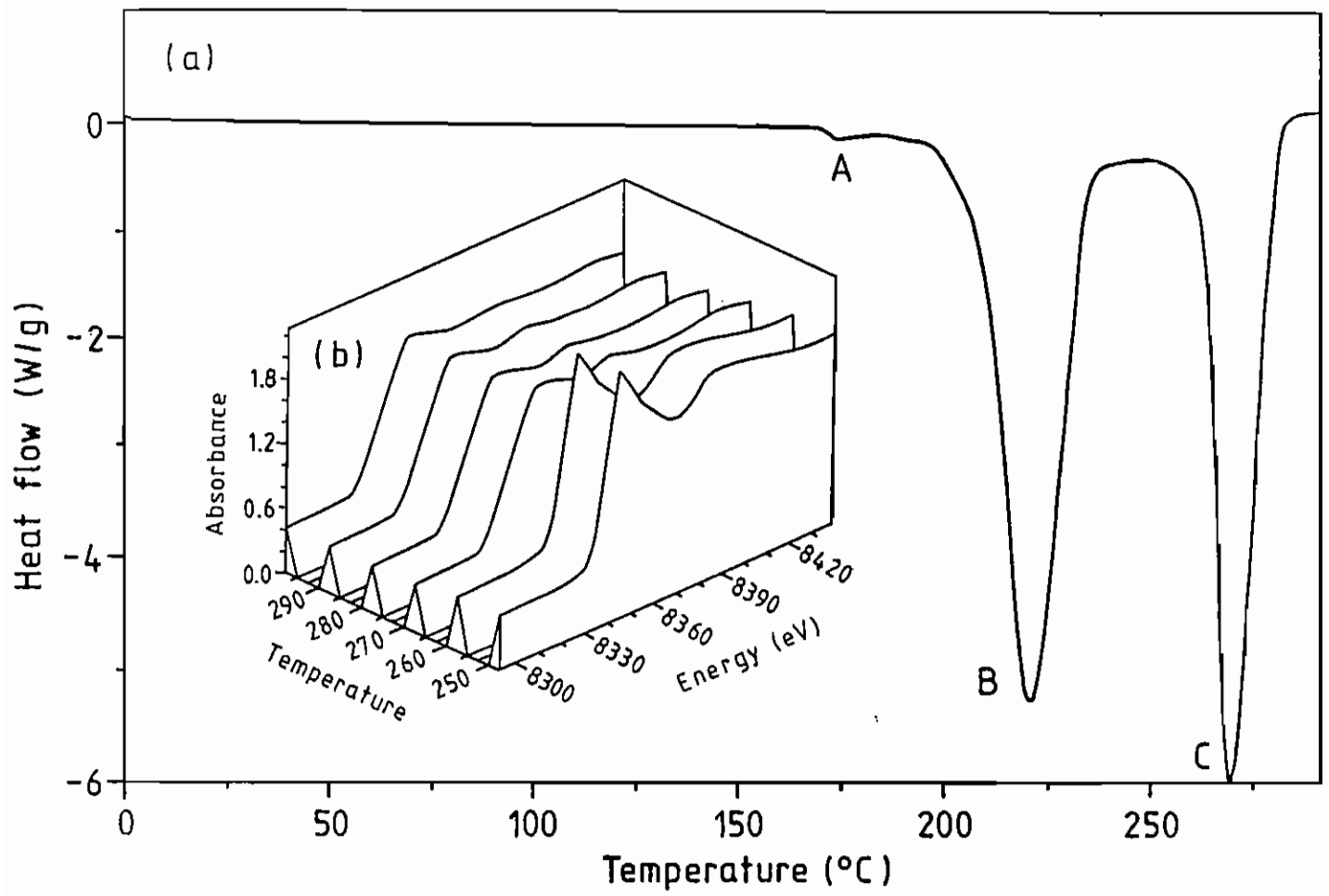


Fig. 3

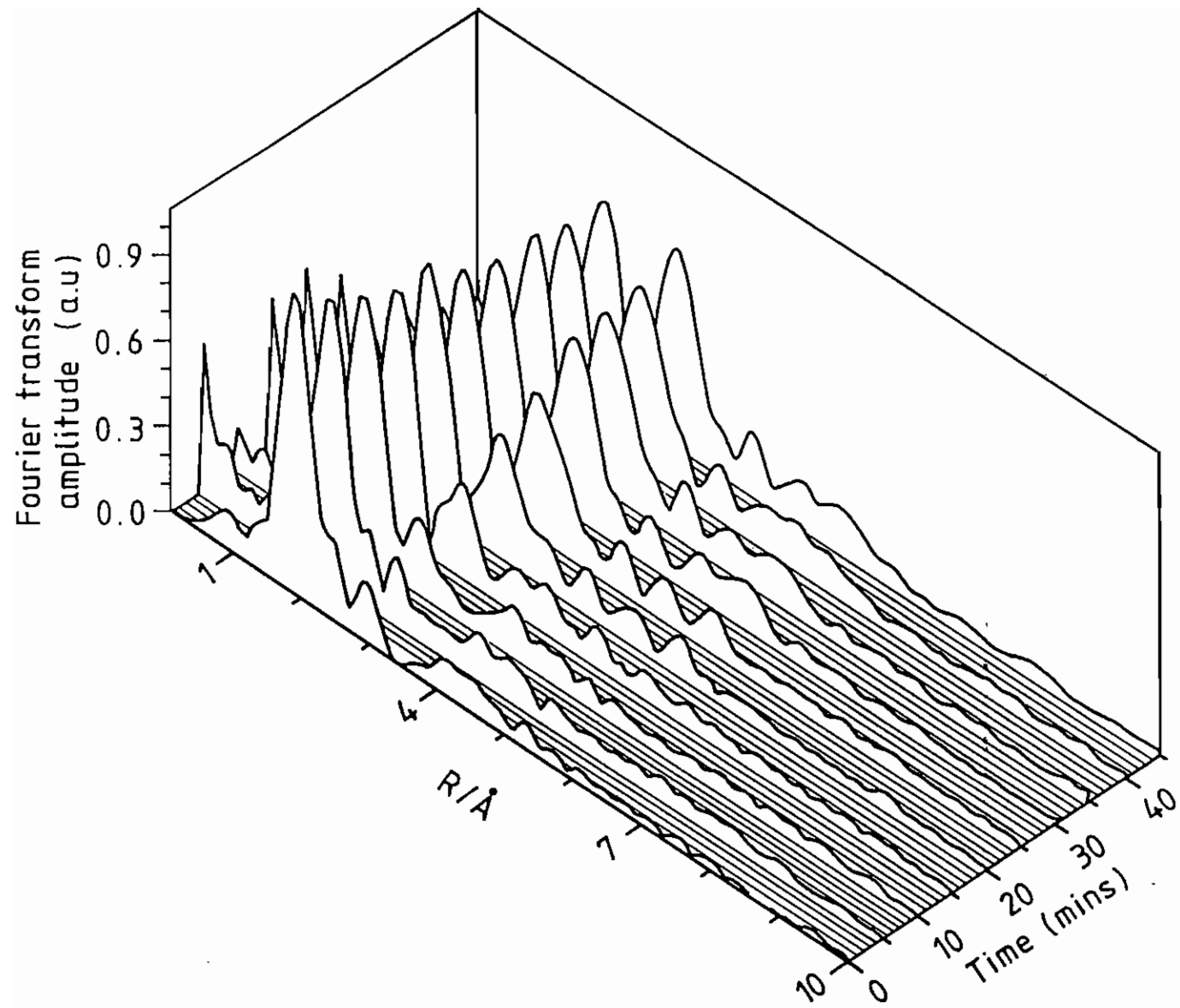


Fig. 3 (c)

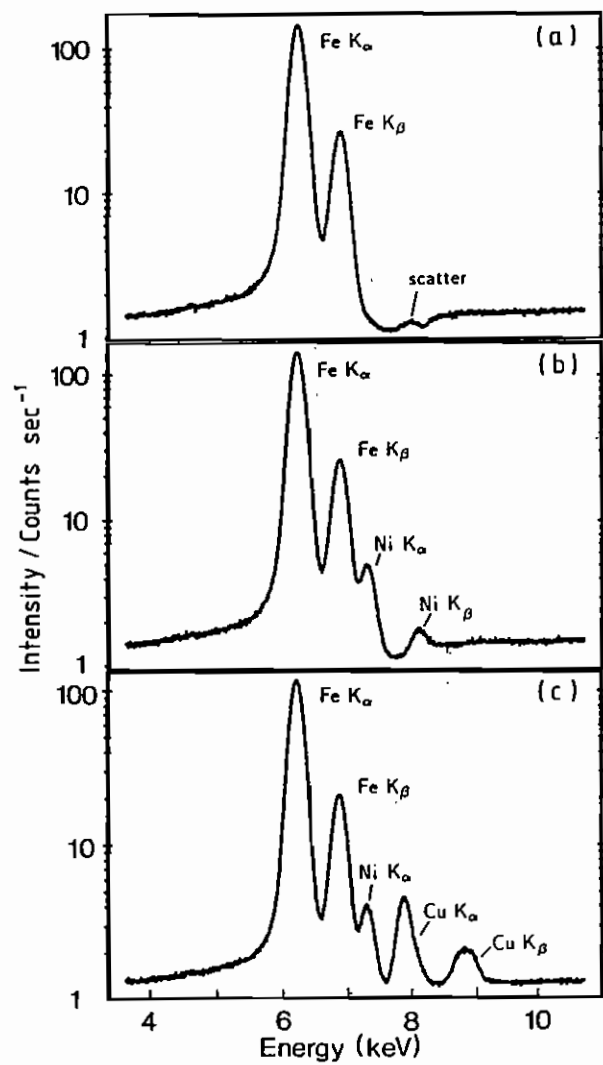


Fig. 4

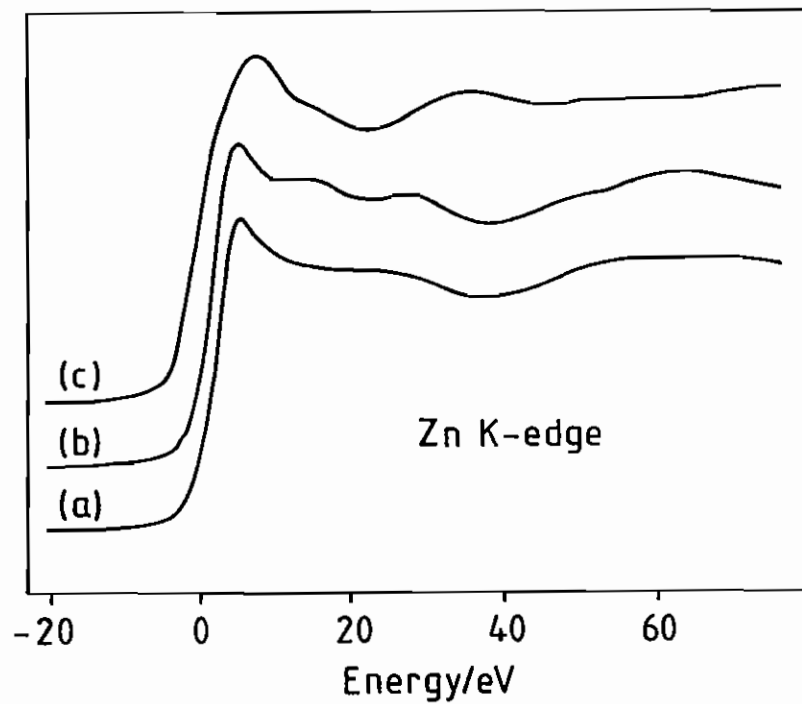


Fig.5

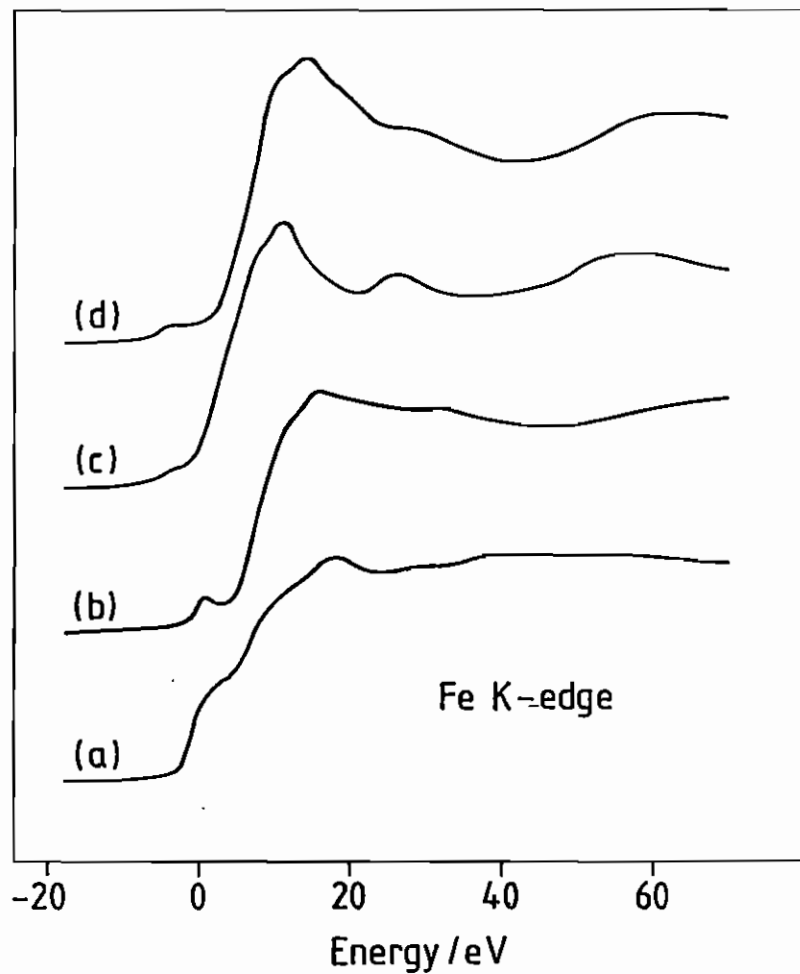


Fig. 6

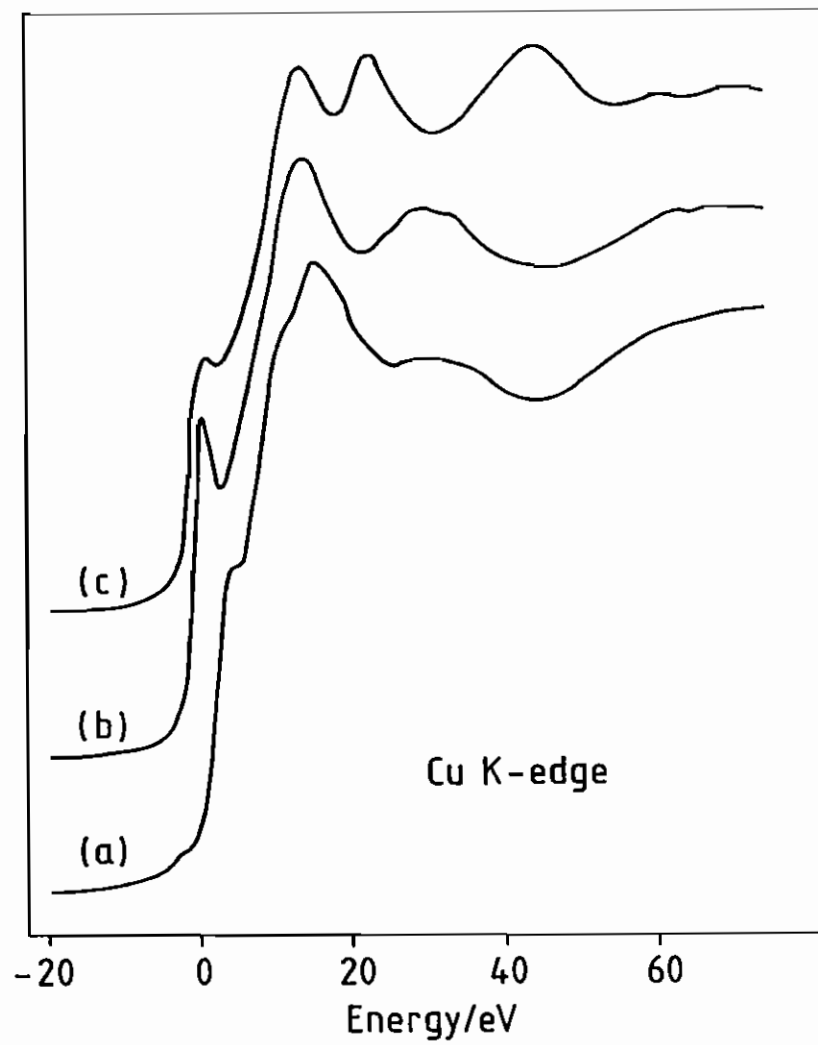


Fig. 7

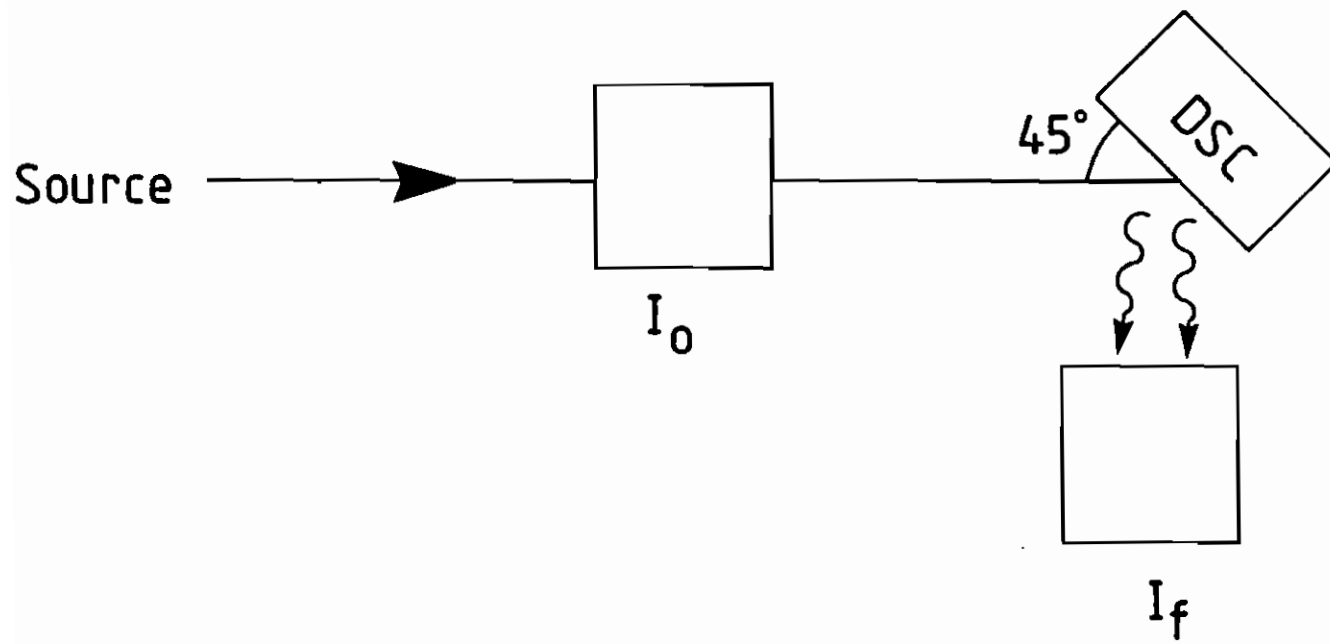


Fig. 8