References

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DISCUSSION

G. E. BACON: Have you any explanation why the observed line widths for nickel lay consistently above —10% or so— the calculated values for the 'parallel' position?

G. CAGLIOTI: The explanation for the small systematic difference between experimental and calculated widths of Bragg reflections for powder samples, appearing in some of the cases we considered, is not easy to be found. That difference seems not to be due to having neglected the vertical angular divergence of the collimators. Besides, in the present experimental conditions, the full width at half maximum vs. the dispersion parameter a does not depend on the mosaic spread of the monochromator.

It should be mentioned at this point that similar measurements, recently reported by Prof. Shull, seem to indicate a small systematic deviation of his results with respect to the theoretical predictions, but in a sense opposite to the one here presented. In fact Shull finds, at large Bragg angles, a better resolution than the one predicted by the theory, at least for large values of the scattering angle $2\theta_B$.

Finally, I would like to remark that any comparison of the predicted resolution with the experimental one should be made with the experimental conditions proposed by the theory, that is using Soller type collimators and standard powder samples.

Neutron Diffraction Work at the Ispra Center

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In this communication we present results recently obtained with the neutron diffraction spectrometer installed at the Ispra-1 reactor on the structure of liquid bromine and cupric oxide.

The neutron diffraction analysis of liquid bromine near the melting point has been carried out up to a very large value of $4\pi \sin\theta/\lambda$. The radial distribution function shows clearly that in the liquid state, at room temperature, the molecules are not freely rotating. Moreover it seems that the main features of the structure of the parent solid, are preserved during the melting process.

The crystal and magnetic structures of copper oxide have been confirmed.

Liquid bromine

The structure of polyatomic liquids has not been so far widely investigated, as much as the structure of monoatomic liquids. While the latter is very important for an under-standing of the general properties of a liquid, the structure of polyatomic liquids is worthwhile to be investigated because of the information one can get about particular aspects of the liquid state, such as, for instance, the
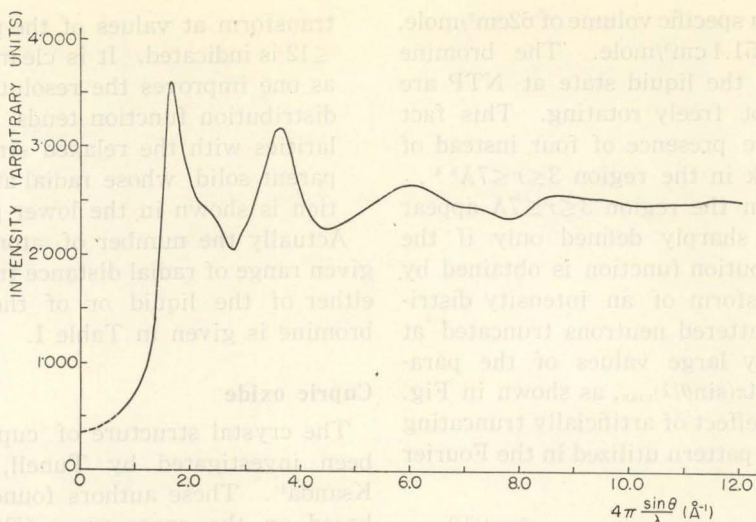
Fig. 1. Neutron diffraction pattern of liquid bromine at room temperature.

meaning of the entropy associated with the process of melting in terms of the achievement of free rotations of the molecules.

Suitable systems to be considered are the halogens. With exception of the chlorine, it seems that no investigations have been reported on liquid halogens.

In this communication we wish to present some results obtained at Ispra on the structure of liquid bromine.

The experimental data have been taken at room temperature and atmospheric pressure utilizing two wavelengths, i. e. 0.75 Å and 0.95Å. They have been corrected for the contribution of the quartz container, and are

Fig. 2. Radial distribution function of liquid bromine.

presented in Fig. 1. It should be remarked that the data extend up to a comparatively high value of the resolution parameter $s = 4\pi\sin\theta/\lambda$, i. e. up to about 12 Å^{-1}.

In order to obtain the radial distribution function from the intensity data, by operating on them with the conventional Fourier transform, we have previously subtracted from any measured value of the intensity the small contribution of multiple and incoherent scattering (supposed to be isotropic) represented by the extrapolated intensity at zero angle.

The radial distribution function so obtained is presented in Fig. 2.

We should observe at this point the following facts:

1) There is a definite peak of area equal to one atom at a distance of 2.3 Å apart from the atom at the origin. Such a peak indicates, also in the liquid state, the existence of bromine as a diatomic molecule. The intermolecular distance Br-Br is 2.30 ± 0.05Å in good agreement with the value of 2.29 Å obtained from measurements in the gaseous state[1], and with the value 2.27 Å obtained from measurements in the solid state[2].

2) The minimum distance of approach of two bromine atoms belonging to different molecules is about 2.96 Å. Consequently, if we suppose the bromine molecules to be freely rotating and pack them in a close packed arrangement (f. c. c.), the liquid made up of freely rotating molecules
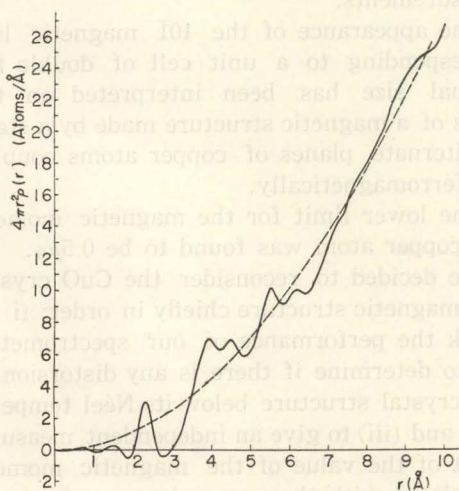
should have a specific volume of 62cm³/mole, instead of 51.4 cm³/mole. The bromine molecules in the liquid state at NTP are therefore not freely rotating. This fact explains the presence of four instead of a single peak in the region $3 \leq r \leq 7\text{Å}$[3,4].

3) The peaks in the region $3 \leq r \leq 7\text{Å}$ appear to be rather sharply defined only if the radial distribution function is obtained by Fourier transform of an intensity distribution of scattered neutrons truncated at comparatively large values of the parameter $s_{max} = 4\pi(\sin\theta/\lambda)_{max}$, as shown in Fig. 3, where the effect of artificially truncating the intensity pattern utilized in the Fourier
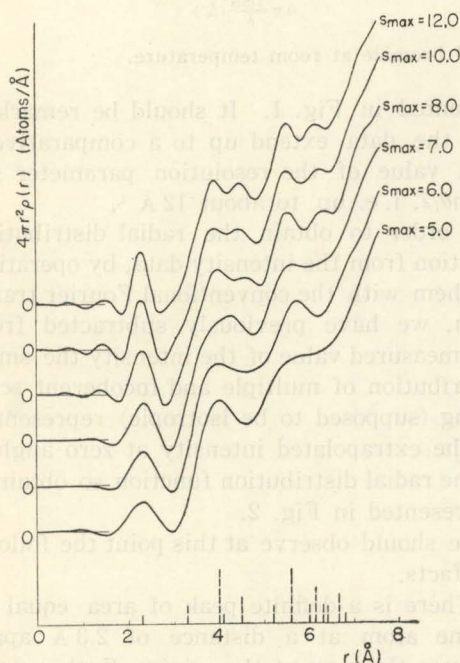

Fig. 3. Radial distribution function of liquid bromine for various cut-offs artificially introduced in the diffraction pattern. The bars in the bottom indicate the number of atoms existing in the solid bromine at any radial distance.

Table I. Number of atoms lying in a given range of radial distance from the origin, both for solid and liquid Bromine.

Range (Å)	3.4–4.3	4.3–5.0	5.2–5.9	6.0–6.7
Solid	7	3	8	13
Liquid	5.5	3.5	7.4	(7)

transform at values of the parameter $s_{max} \leq 12$ is indicated. It is clearly shown that, as one improves the resolution, the radial distribution function tends to show similarities with the relaxed structure of the parent solid, whose radial atomic distribution is shown in the lower part of Fig. 3.

Actually the number of atoms lying in a given range of radial distance from the origin either of the liquid or of the parent solid bromine is given in Table I.

Cupric oxide

The crystal structure of cupric oxide has been investigated by Tunell, Posnjak and Ksanda[5]. These authors found a structure based on the space group $C2/c$, with atoms placed in special positions. Bond distances and bond angles depend upon the only parameter of the structure, i.e. the u parameter of the oxygens along the unique b-axis of the monoclinic unit cell. The given value, $u = 0.416 \pm 0.01$, corresponds to an arrangement of atoms in a four coordination, each oxygen being surrounded, at equal distances, by four copper atoms at the corners of a non-equilateral tetrahedron, and each copper atom being surrounded, at equal distances by four oxygens lying in a plane at the corners of a rectangle (OCuO angles $\neq 90°$).

Brockhouse[6] found, by neutron diffraction, an antiferromagnetic transition at $T_N \simeq 220°K$ and such transition has been related, by Bizette and Tsaï[7], to magnetic susceptibility measurements.

The appearance of the $10\bar{1}$ magnetic line corresponding to a unit cell of double the normal size has been interpreted on the basis of a magnetic structure made by a stack of alternate planes of copper atoms coupled antiferromagnetically.

The lower limit for the magnetic moment per copper atom was found to be $0.5\mu_B$.

We decided to reconsider the CuO crystal and magnetic structure chiefly in order: (i) to check the performance of our spectrometer, (ii) to determine if there is any distorsion of the crystal structure below its Néel temperature and (iii) to give an independent measurement of the value of the magnetic moment associated with the copper ion.

In particular, point (ii) is directly connected with the Jahn-Teller[8] effect for non-sym-
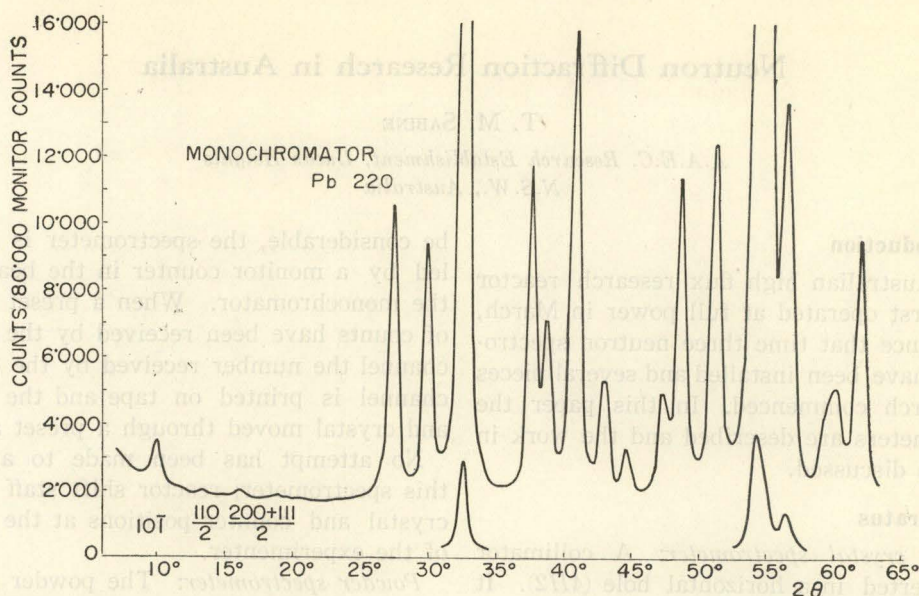
Fig. 4. Neutron diffraction pattern of cupric oxide at liquid nitrogen temperature. The value $\lambda=1.29_5$ Å was selected in order to improve the resolution.

metrical "d" electron configuration.

Fig. 4 shows the CuO powder diffraction pattern taken at 80°K, using $\lambda=1.29_5$Å. The pattern can be indexed on the basis of the TPK[5] unit-cell, with the exception of the first reflection, which can be indexed as the 10$\bar{1}$ reflection of a unit cell doubled.

This reflection is, evidently, the magnetic line investigated by Brockhouse.

The best agreement between calculated and observed intensities is obtained for $u=0.416$. It follows that the crystal structure remains practically unchanged below the Néel temperature.

Our diffraction pattern shows no evidence of other magnetic lines besides 10$\bar{1}$.

In agreement with Brockhouse[6], the appearence of the 10$\bar{1}$ magnetic line can be explained assuming that alternate planes 20$\bar{2}$ of the crystal structure, are coupled antiferromagnetically.

At present further investigations are in progress in order to get more accurate information on point (iii).

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