geometrical factors to obtain adequate resolution; on the avoidance of fluorescence that can saturate the present generation of energy-dispersive detectors and thereby swamp the diffuse scattering. The first and last of these points introduce significant extra difficulties with white radiation over the use of monochromatic X-rays or neutrons.

The most promising applications are with light-element materials, where the absorption of adequately sized samples is modest for wavelengths below 1 Å and their fluorescence above 2 Å is either beyond the energy response of the detector or can be readily blocked by a thin filter. Harada *et al.* (1984) have demonstrated that applications are also possible with heavy-element materials, where the *K* fluorescence is too hard to be excited and the *L* fluorescence can be tolerated. Paper II of this series will discuss results obtained using light elements.

The author would like to thank the Science and Engineering Research Council for grant support during the development of this subject; staff at the Daresbury Synchrotron Radiation Laboratory for their encouragement, particularly Phil Pattison (now developing facilities at ESRF); at Aberdeen University, John D. Pirie and Stephen D. Clackson for discussions during the practical development of the technique, which will be illustrated in paper II.

References

CRC Handbook of Chemistry and Physics (1972). Boca Raton, Florida: Chemical Rubber Co.

HARADA, J., IWATA, H. & OHSHIMA, K. (1984). *J. Appl. Cryst.* **17**, 1-6.

HASEGAWA, K., MOCHIKI, K., KOIKE, M., SATOW, Y., HASHIZUME, H. & IITAKA, Y. (1986). *Nucl. Instrum. Methods Phys. Res.* A**252**, 158-168.

HOWELLS, G. (1950). *Acta Cryst.* **3**, 366-369.

International Tables for X-ray Crystallography (1983). Vol. III, pp. 171-173. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

IWASAKI, H., MATSUO, Y., OHSHIMA, K. & HASHIMOTO, S. (1990). *J. Appl. Cryst.* **23**, 509-514.

IWASAKI, H., SASAKI, S., KISHIMOTO, S., HARADA, J., SAKATA, M., FUJII, Y., HAMAYA, N., HASHIMOTO, S., OHSHIMA, K. & OYANAGI, H. (1989). *Rev. Sci. Instrum.* **60**, 2406-2409.

JAGODZINSKI, H. (1987). *Prog. Cryst. Growth Charact. Mater.* **14**, 47-102.

KRUMREY, M., TEGELER, E. & ULM, G. (1989). *Rev. Sci. Instrum.* **60**, 2287-2290.

LAL, K. (1989). *Prog. Cryst. Growth Charact. Mater.* **18**, 227-266.

LAUNDY, D., CUMMINGS, S. & PATTISON, P. (1991). *Nucl. Instrum. Methods Phys. Res.* A**302**, 553-557.

LAUNDY, D., CUMMINGS, S., PATTISON, P., HONKIMÄKI, V. & SLEIGHT, J. (1990). Daresbury Annual Report 1989/1990, Appendix, p. 164. SERC Daresbury Laboratory, Warrington, England.

MAETA, H., LARSON, B. C., SJOREEN, T. P., THOMAS, D. K., OEN, O. S. & LEWIS, J. D. (1988). *Mater. Res. Soc. Symp. Proc.* **138**, 81-86.

MATSUBARA, E. & GEORGOPOULOS, P. (1985). *J. Appl. Cryst.* **18**, 377-383.

MEULENAER, J. DE & TOMPA, H. (1965). *Acta Cryst.* **19**, 1014-1018.

OSBORN, J. C. & WELBERRY, T. R. (1990). *J. Appl. Cryst.* **23**, 476-484.

REID, J. S. (1981). *Acta Cryst.* A**37**, 382-390.

REID, J. S. (1989). *Comput. Phys. Commun.* **54**, 307-314.

SHULTZ, H. (1982). *Current Topics in Materials Science*, Vol. 8, edited by E. KALDIS, pp. 277-379. Amsterdam: North-Holland.

WELBERRY, T. R. (1985). *Rep. Prog. Phys.* **48**, 1543-1593.

Acta Cryst. (1993). A**49**, 198-202

Ferroelectric Phase Transition in $Li_2Ge_7O_{15}$ Investigated by Mössbauer Diffraction

BY K. KREC AND W. STEINER

Institut für Angewandte und Technische Physik, Technische Universität Wien, Austria

AND M. WADA*

Synthetic Crystal Research Laboratory, Nagoya University, Nagoya, Japan

(*Received* 11 *October* 1991; *accepted* 24 *July* 1992)

Abstract

Mössbauer diffraction experiments were performed on a single crystal of lithium heptagermanate in the temperature range 250-350 K. The high energy resolution of resonant γ radiation was used to separate elastically and inelastically scattered components. A lattice expansion along **c** and a decrease of the intensity of the elastically scattered radiation (I_{Bragg}) connected with an increase of the intensity of the inelastically scattered radiation (I_{TDS}) are observed at the transition from the para- to the ferroelectric phase at 283.5 K. The experimentally determined maximum of I_{TDS}/I_{Bragg} appearing at the phase transition is much more pronounced in comparison with

* Present address: Department of Physics, Faculty of Liberal Arts, Shinshu University, Matsumoto, Japan.

0108-7673/93/010198-05$06.00

that predicted from TDS-correction programs, which are based on the lattice dynamical theory restricted to acoustic phonons only.

I. Introduction

Crystals of lithium heptagermanate, $Li_2Ge_7O_{15}$ (subsequently referred to as LGO) were the subject of detailed investigation concerning the ferroelectric phase transition that occurs at $T_c = 283.5$ K (Haussühl, Wallrafen, Recker & Eckstein, 1980). Raman scattering experiments (Wada & Ishibashi, 1983) and far-infrared studies (Sawada, Wada, Fujita & Toibana, 1985) performed on single crystals of LGO indicated that the phase transition is associated with a soft optical phonon. Neutron diffraction studies (Iwata, Shibuya, Wada, Sawada & Ishibashi, 1987) indicated that this phonon is connected with the quenching of the tilting motion of the GeO_4 tetrahedra, which share their corners with the GeO_6 octahedra. The paraelectric phase is characterized by anisotropic thermal motions with the c axis of vibration aligned between the two ferroelectric configurations. In particular, one of the Li atoms exhibits a large anisotropy of the thermal parameters and its behaviour at the transition may be better explained by an 'order-disorder' model than by a 'displacive' one. In the ferroelectric phase all atoms are well described by thermal isotropic parameters.

The use of Mössbauer radiation in a scattering experiment offers the possibility to separate (with an energy resolution of 10^{-9} eV) elastically and inelastically scattered radiation (O'Connor & Butt, 1963). In addition to this separation the inelastically scattered radiation can be separated from the background component using an energy-dispersive mode of registration (Krec & Steiner, 1984). Integrated intensities for both the inelastically and the elastically scattered contributions can be determined separately from the dependence of the measured intensities on the scattering angle for fixed scan lengths.

In the course of such measurements performed at room temperature on a single crystal of LGO around the 009 reflection, only thermal diffuse scattering (I_{TDS}) was observed but not elastically scattered intensity (I_{Bragg}). This supports *Pbcn* as the space group for the paraelectric phase of LGO (Krec & Steiner, 1986). For the 0,0,10 reflection at room temperature, agreement was obtained between the measured and calculated dependences of the ratio of thermally diffuse to elastically scattered radiation (I_{TDS}/I_{Bragg}) on the scan length for scan lengths below 0.7°. For the calculations, the TDS-correction programs written by Stevens (1974), Helmholdt & Vos (1977) and Kurittu & Merisalo (1977) were used (Krec, 1989).

It was the aim of the present investigation to check whether this agreement for I_{TDS}/I_{Bragg} is valid for a larger temperature range and whether lattice dynamical theory based on acoustic phonon dispersion (see, for example, Willis & Pryor, 1975), which is used for the TDS-correction programs, is capable of explaining the measured ratio of I_{TDS}/I_{Bragg} for the whole temperature range for which elastic constants are available. The results indicate that, even in a narrow temperature interval around T_c, large discrepancies between calculated and measured ratios occur. Furthermore, the scattered intensity of the 0,0,10 reflection is predominantly generated by the Ge atoms. A detailed investigation of the elastic intensity in the region around the transition temperature will therefore help to obtain additional information about the nature of the transition.

II. Experimental details

The measurements were performed on a plane parallel plate of a single crystal of LGO in asymmetric Bragg geometry. The angular dependences of both the elastically and the inelastically scattered radiation in the region of the 0,0,10 reflection were determined by means of θ-2θ scans at different temperatures between 250 and 355 K. The temperature was controlled by a continuous-flow cryostat and measured with an Au-Fe thermocouple. A temperature stability of ±0.05 K was achieved during the time necessary to obtain sufficient counting statistics (usually three weeks for each particular temperature). The absolute accuracy of the calibration for the thermocouple in the temperature range used was ±0.1 K. The divergence of the used beam (source ^{57}FeRh) was 0.65° in the horizontal and 1.40° in the vertical direction. The counter aperture was 10 mm in diameter, corresponding to a divergence of 3.45°. Further details of the experimental setup are described elsewhere (Krec & Steiner, 1984).

The elastic constants necessary for the calculations were taken from Haussühl *et al.* (1980) for the temperature range 253-303 K. For the paraelectric phase, the space group (*Pbcn*) and the lattice constants are given by Völlenkle, Wittmann & Nowotny (1970) and Terauchi, Iida, Nishihata, Wada, Sawada & Ishibashi (1983). For the ferroelectric phase, the space group ($Pbc2_1$) is taken from Iwata *et al.* (1987).

III. Results and discussion

The intensities of elastically and inelastically scattered radiation and the background contribution were measured in the angular range $\theta = 25.5$-$26.5°$ (Fig. 1). In addition to this, the inelastic and background contributions were also determined for $\theta = 25$ and 27°, somewhat away from the Bragg position. Subsequently, the temperature dependence of the line positions as well as of the integrated Bragg and TDS intensities are presented and discussed.

A. Line position

The angular dependence of the intensity of the elastically scattered radiation was fitted by means of a Gaussian for all temperatures. The line position was determined from the maximum of this distribution function and further used to calculate the lattice constant c (Fig. 2).

For both the ferro- and the paraelectric state a linear increase of the lattice constant c with increasing temperature is observed. This temperature dependence is in agreement with known results for the thermal expansion (Wada & Ishibashi, 1983). A maximum was observed for c around the phase-transition temperature (Fig. 2). To our knowledge, the temperature dependence of the lattice parameters has not yet been determined (*e.g.* by X-ray investigations). In the present experiments, the samples used are much smaller than those used for the thermal expansion experiments and, because of the long measuring time necessary to get reasonable counting statistics, the temperature distribution in the crystal is very homogeneous. These are probably the reasons why the maximum of c was not detected in the thermal-expansion measurements. From the present experiments it must therefore be concluded that the phase transition at 283.5 K is linked to a marked expansion of the lattice in the c direction.

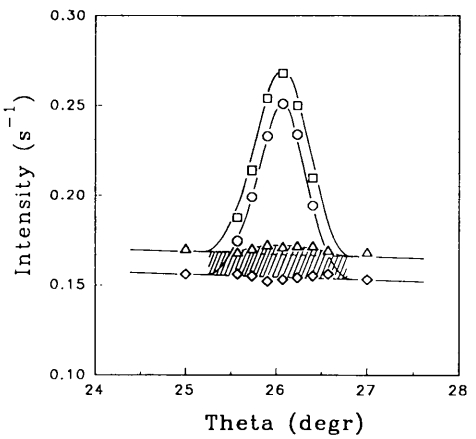

Fig. 1. 0,0,10 reflection of LGO at room temperature. Inelastic (△), elastic (○) and total (□) intensity. Full curves calculated by means of a Gaussian distribution function. Background (◇), full curve: linear regression. Shaded area: integrated thermally diffuse scattered intensity (I_{TDS}).

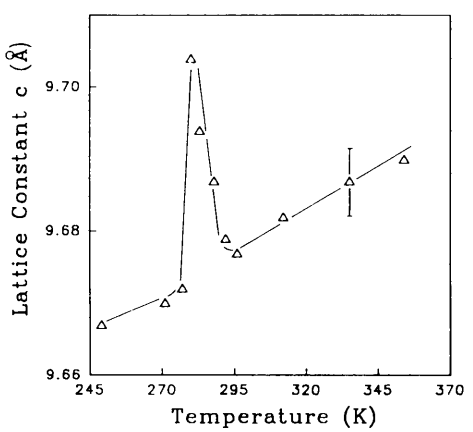

Fig. 2. Temperature dependence of the lattice constant c for LGO.

B. Integrated intensities

The angular dependence of the intensity of the measured inelastically scattered radiation (I_{TDS}) was fitted by means of a superposition of a linear function and a Gaussian at the Bragg position (Fig. 1). For all investigated temperatures an inelastic contribution is present above the background, even far away from the Bragg peak. To determine the integrated intensity of the inelastically scattered radiation, it is therefore necessary to fix the angular range used for the integration (scan length). As mentioned above, detailed investigations on the same crystal at room temperature show that, for the ratio of thermally diffuse to elastically scattered radiation (I_{TDS}/I_{Bragg}), an agreement between experiment and calculation is only present for scan lengths less than 0.7° (Fig. 3). For larger scan lengths the long-wavelength approximation is no longer valid and the exact phonon-dispersion relation should be taken into account in the calculations. This result was used as a criterion since the aim of the present investigation was a check of this agreement at different temperatures. Therefore a scan length of 0.6° was chosen for the determination of the integrated inelastically scattered intensities.

In the investigated temperature interval for the 0,0,10 reflection of LGO, I_{Bragg} is of the same order for the ferro- and the paraelectric phases and decreases approximately linearly with increasing temperature (Fig. 4). Only within a narrow temperature range around the phase transition is a drastic decrease

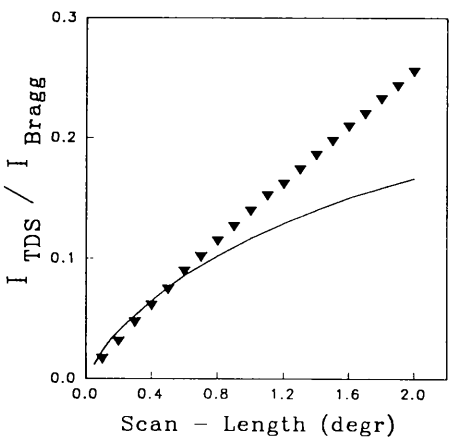

Fig. 3. Dependence of I_{TDS}/I_{Bragg} on the scan length for the 0,0,10 reflection of LGO at room temperature. ▼ Experiment; —— calculated by means of TDS-correction program *TDS*1/4 (Helmholdt & Vos, 1977).

of I_{Bragg} observed. Within the same temperature range, a distinct increase of the integrated inelastically scattered intensity is visible, whereas it changes only smoothly in other temperature regions.

The temperature dependence of the intensity of scattered X-radiation for the same reflection was investigated by Terauchi *et al.* (1983). In these investigations, the change in intensity around the transition temperature was not observed. In a conventional X-ray experiment, a separation of I_{Bragg} and I_{TDS} is not possible, in contrast to the present experiment. Since the two contributions influence the total intensity in opposite ways, the decrease of the elastically scattered intensity may not be easily detectable within ordinary X-ray investigations.

From the results obtained at room temperature (Krec, 1989), it is assumed that the main part of the inelastically scattered radiation is caused by thermal diffuse scattering. This assumption is supported by the fact that, in agreement with I_{TDS}, the elastic constants, determined by means of ultrasonic measurements, also exhibit large changes at the phase transition (Haussühl *et al.*, 1980).

To confirm that the increase of I_{TDS} can be explained by a change of the dispersion relation of the acoustic phonons, the temperature dependence of the ratio I_{TDS}/I_{Bragg} was calculated for different crystal temperatures by means of the elastic constants given by Haussühl *et al.* (1980). The TDS-correction program *TDS*1/4 (Helmholdt & Vos, 1977) was used for the calculations; it is based on the kinematical approximation. Therefore, to compare these values with the experimentally determined ones, the measured integrated Bragg intensity of the used perfect single crystal was divided by the extinction factor, which was calculated from the dynamical theory, to obtain the intensities for the kinematical approximation. The computer program necessary for the determination of the extinction factor is based on the equations given by Batterman & Cole (1964) and also allows calculations for asymmetric Bragg geometry and crystals without a centre of symmetry (Krec, 1989).

The calculated and measured temperature dependences of I_{TDS}/I_{Bragg} are compared in Fig. 5. For both the para- and the ferroelectric phases, good agreement between theory and experiment is observed within the chosen scan length for temperatures that are not too close to T_c. However, the maximum of I_{TDS}/I_{Bragg} appearing at the phase transition is experimentally much more pronounced compared with theory. The strong decrease of the elastic intensity in the temperature range around the phase transition, which is ignored within the TDS-correction program, is not able to explain the large discrepancy. This can be easily seen if, instead of the calculated values of I_{Bragg}, the experimentally determined ones are used for the calculations. A change of the slope of acoustic branches of the phonon-dispersion relation alone is not able to explain the observed increase of I_{TDS}/I_{Bragg}.

In the paraelectric phase of LGO, the B_{1u} soft phonon mode was observed and, in the ferroelectric phase, the corresponding A_1 mode was observed. The soft phonon has a small oscillator strength and its contribution to the dielectric constant does not exceed 0.1 even in the vicinity of T_c (Wada, Fujita, Sawada & Ishibashi, 1985). However, the temperature dependence of the dielectric constant measured along the c axis (Wada & Ishibashi, 1983) exhibits a strong increase in the same narrow temperature interval in which the increase of c and the decrease of I_{Bragg} are observed. In the approach to T_c from above, an expansion of the lattice (at least in the c direction)

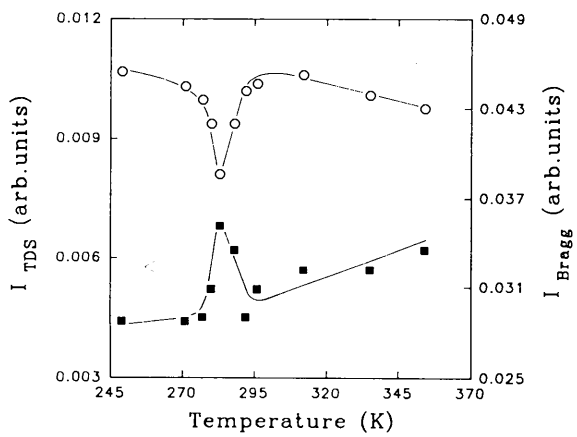

Fig. 4. Temperature dependence of elastically (I_{Bragg}, ○) and inelastically (I_{TDS}, ■) scattered integrated intensity for the 0,0,10 reflection of LGO.

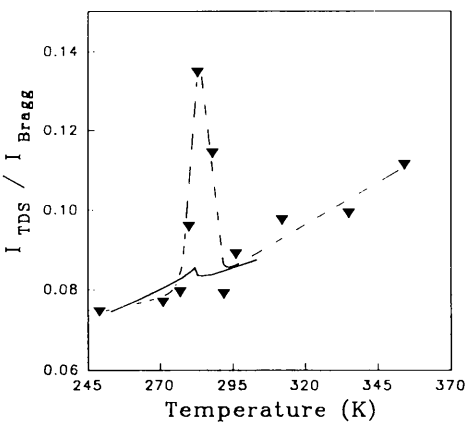

Fig. 5. Temperature dependence of measured (▼) and calculated (solid line) ratio I_{TDS}/I_{Bragg}. For details see text. The dashed line is only a visual guide.

occurs, which immediately relaxes by a reduction of the temperature below T_c. Hence, the strong growth of the intensity of the inelastically scattered radiation and the resulting increase of I_{TDS}/I_{Bragg} in the immediate vicinity of T_c seem to be a further hint that the phase transition is associated with the softening of an optical phonon and that at T_c a relaxational mode becomes of great importance (Wada *et al.*, 1985). Since the elastic intensity of the 0,0,10 reflection is dominated by the scattering of the Ge atoms and the contributions of both Li and O atoms are very small, the decrease in the elastic intensity in this small temperature interval around T_c indicates that immediately at the transition temperature the motion of the Ge atoms also becomes important. From the present experiments it is not possible to decide whether this decrease is caused by an increase of the Debye-Waller factor or by a displacive motion of the Ge atoms or how this behaviour is connected to the motion of the Li atoms. Since, however, in both the para- and the ferroelectric phases the equilibrium positions of the Ge atoms are nearly the same (Iwata *et al.*, 1987), a displacement seems to be less probable. The present measurements show for the first time that a lattice expansion in the *c* direction and a decrease of the elastically scattered intensity connected with an increase of the inelastically scattered intensity appears at the phase transition of LGO.

References

BATTERMAN, B. W. & COLE, H. (1964). *Rev. Mod. Phys.* **36**, 681-717.

HAUSSÜHL, S., WALLRAFEN, F., RECKER, K. & ECKSTEIN, J. (1980). *Z. Kristallogr.* **153**, 329-337.

HELMHOLDT, R. B. & VOS, A. (1977). *Acta Cryst.* A**33**, 38-45.

IWATA, Y., SHIBUYA, I., WADA, M., SAWADA, A. & ISHIBASHI, Y. (1987). *J. Phys. Soc. Jpn*, **56**, 2420-2427.

KREC, K. (1989). Thesis, TU Wien, Austria.

KREC, K. & STEINER, W. (1984). *Acta Cryst.* A**40**, 459-465.

KREC, K. & STEINER, W. (1986). *Hyperfine Interact.* **29**, 1351-1353.

KURITTU, J. & MERISALO, M. (1977). *Report Series in Physics*, No. 132. Univ. of Helsinki, Finland.

O'CONNOR, D. A. & BUTT, N. M. (1963). *Phys. Lett.* **7**, 233-235.

SAWADA, A., WADA, M., FUJITA, K. & TOIBANA, H. (1985). *Jpn. J. Appl. Phys.* **24**, 534-535.

STEVENS, E. D. (1974). *Acta Cryst.* A**30**, 184-189.

TERAUCHI, H., IIDA, S., NISHIHATA, Y., WADA, M., SAWADA, A. & ISHIBASHI, Y. (1983). *J. Phys. Soc. Jpn*, **52**, 2312-2314.

VÖLLENKLE, H., WITTMANN, A. & NOWOTNY, H. (1970). *Monatsh. Chem.* **101**, 46-56.

WADA, M., FUJITA, K., SAWADA, A. & ISHIBASHI, Y. (1985). *Jpn. J. Appl. Phys.* **24**, 488-490.

WADA, M. & ISHIBASHI, Y. (1983). *J. Phys. Soc. Jpn*, **52**, 193-199.

WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, pp. 232-239. Cambridge Univ. Press.

Acta Cryst. (1993). A**49**, 202-208

New Aspects in the Theory of the Double Kink on a Dislocation

BY M. E. POLYAKOV

B. I. Stepanov Institute of Physics, BSSR Academy of Sciences, Leninsky prospekt 70, 220602 *Minsk, Byelorussia*

(*Received* 26 *October* 1991; *accepted* 3 *August* 1992)

Abstract

A theory of the double kink on a dislocation that is free of the disadvantages of previous models has been developed. In this theory the force of external action is assumed to be equal to the Peierls barrier reaction.

Introduction

As concluded by Imai & Sumino (1983), none of the reported theoretical models can explain the measured dislocation velocities. They used a high-power Röntgen generator for measurements *in situ* of dislocation mobility at elevated temperatures over a wide range of stresses in pure and doped silicon crystals. In particular, it was shown that a change of dislocation velocity with stresses for screw and 60° dislocation in highly pure crystals will be linear over the whole range of the investigated stresses and that the activation energy for the dislocation mobility does not depend on stresses.

According to Imai & Sumino (1983), the main disadvantage of previously reported experimental studies was that dislocation mobility measurements were made at elevated temperatures due to heating and cooling of a sample from room temperature to the temperatures of investigations. The distinguishing feature of the present work is that it overcomes the limitations of earlier works and makes investigations at a fixed temperature.

At the present time there are two basic theories of dislocation propagation in crystals with high Peierls barriers: the diffusion and the obstacle theories. According to the diffusion theory, a full dislocation

0108-7673/93/010202-07$06.00